X-RAY CRYSTAL STRUCTURE ANALYSES OF A SULTONE AND SOME DITERPENOIDS

A thesis submitted to the University of Glasgow for the degree of Doctor of Philosophy in the Faculty of Science

by

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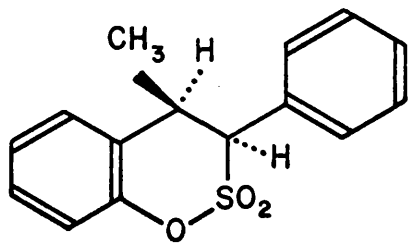
Summary

This thesis is divided into two parts, one theoretical (Part I) and the other experimental (Part II). The first part deals with the theory of X-ray diffraction and with various methods for determination and refinement of structures. Some of these methods have been applied in the study of four organic compounds. This is described in the experimental section.

The study of sultone B, $C_{15}H_{14}O_3S$, was undertaken in order to determine the partially unknown configuration and to obtain accurate molecular dimensions. The structure was found to be

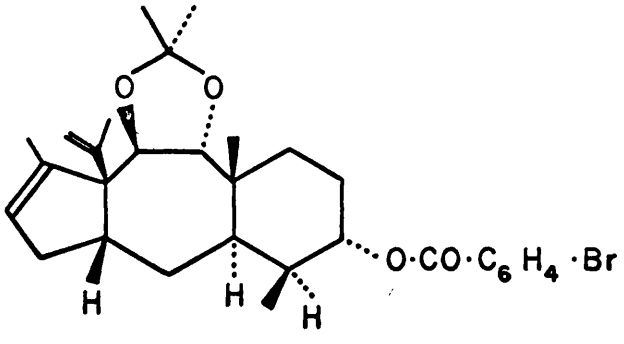


where the heterocyclic ring is in a distorted half-chair conformation with the phenyl group axial and *cis* to the methyl group, which is quasi-equatorial. Some bond lengths are: S-O (peripheral) 1.431 ± 0.003, S-O(C) 1.595 ± 0.004,

S-C 1.797 ± 0.005 and C_{sp^2}-O 1.426 ± 0.005 Å.

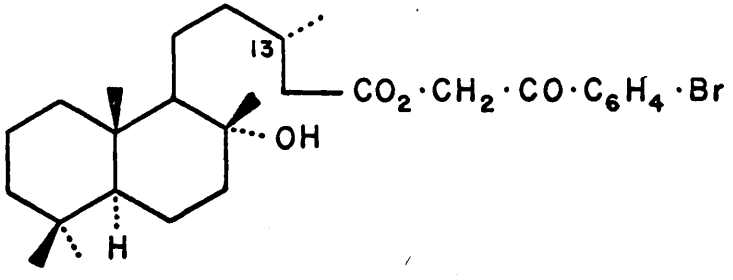
Three derivatives, one of a diterpene and two of diterpenoids, were studied in order to establish their structures and/or stereochemistry. The determinations were all sufficiently accurate to allow fairly detailed discussions of bond lengths and angles. Steric strain, which causes conformational distortions, has been observed in all three structures. The bond angles are influenced appreciably by this effect while only a few bond lengths are affected by it.

Taxadienetetraol, $C_{20}H_{32}O_4$, a new diterpene, was isolated from yew heartwood (*Taxus baccata* L.) by Dr. Halsall's group. The crystal structure and absolute configuration of the p-bromobenzoate of a dihydro-anhydro-acetonide derivative of taxadienetetraol, $C_{30}H_{39}O_4Br$, was found to be



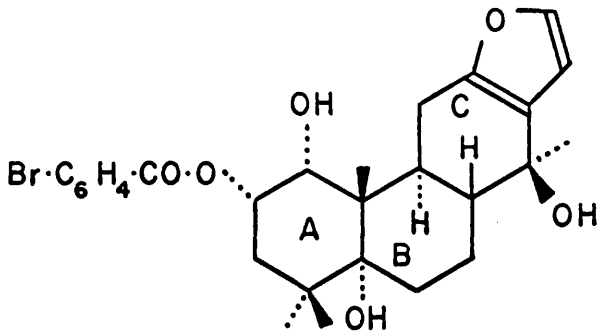
During the formation of this derivative an unexpected rearrangement of the taxane skeleton took place. The derivative contains a five-, a six- and a seven-membered carbon ring in contrast to the two six- and one eight-membered rings of the parent tetraol. The cyclohexane ring adopts the chair form. It is *trans*-fused to the cycloheptane ring which occurs in a twisted boat conformation. The envelope-shaped cyclopentene ring and the acetonide ring in the half-chair form are, respectively, *cis*- and *trans*-fused to the cycloheptane ring.

Labdanolic and eperuic acids have the same configuration at C(13), being otherwise antipodal. The common configuration at C(13) was undefined. The crystal structure of the p-bromophenacyl ester of labdanolic acid, $C_{28}H_{41}O_4Br$, was found to be



The configuration at C(13) was thus established to be (S) (Prelog's notation). The two six-membered rings in the decalin system occur in the chair form and are *trans*-fused to each other.

The analysis of the crystal structure and absolute configuration of a p-bromobenzoate derivative of the diterpenoid ε-caesalpin, $C_{27}H_{33}O_6Br$, gave the following result



The three six-membered rings are fused to form a *trans-anti-trans* system. Rings A and B occur in the chair form while the unsaturated ring C adopts a distorted half-chair conformation. An intramolecular hydrogen bond (2.649 Å) between the two 1,3-diaxial hydroxyl groups was found.

PART I

SOME ASPECTS OF X-RAY DIFFRACTION

1. Introduction

The crystal lattices, symmetry elements, and the classification of crystals in space groups were developed on theoretical grounds long before any experimental data on the subject were available. Before the turn of the twentieth century it was also known that X-rays are produced when high-energy electrons collide with matter. Their wavelengths were assumed to be of the same order of magnitude as the dimensions of chemical molecules. This led von Laue in 1912 to the discovery that X-rays are diffracted by crystals. This achievement was the starting point of a new scientific field in crystallography and soon the study of the internal structure of crystals by X-ray diffraction methods was developed. The results from crystal structure determinations, containing information about the three-dimensional arrangement of atoms as well as interatomic distances and angles, have contributed a great deal to the development and understanding of chemistry.

In the early days the progress was mainly in the field of ionic crystals. With the development of new methods for determining the relative phases of the diffracted waves, more and more complicated structures are

being solved. The calculations necessary for the determination of even a medium large structure are extensive. The computational difficulties have been greatly reduced by the introduction of electronic computers which made possible the solution of structures as complicated as proteins, a previously unimaginable task.

2. Diffraction by a lattice

Consider a lattice with an electron at each lattice point and a beam of monochromatic X-rays of wavelength λ to be incident on this lattice in a direction defined by the unit vector $\underline{s}_o$ with a magnitude $1/\lambda$ (Fig. 1). The scattered wave is defined by the unit vector $\underline{s}$ and under the assumption that only coherent scattering occurs, $\underline{s}$ has the same magnitude as $\underline{s}_o$. The path difference between two scattered waves, one at the origin O and the other at a point A is

$$OB-AC = \lambda (\underline{r}\cdot\underline{s} - \underline{r}\cdot\underline{s}_o) = \lambda \underline{r}\cdot\underline{S} \qquad (1)$$

where $\underline{S} = \underline{s}-\underline{s}_o$ is the scattering vector. The electrons at O and A are separated by $\underline{r} = u\underline{a} + v\underline{b} + w\underline{c}$ where $\underline{a}$, $\underline{b}$, and $\underline{c}$ are the lattice constants and u, v, and w are integers. The scattering from O and A will be in phase when the path difference is equal to a whole number of

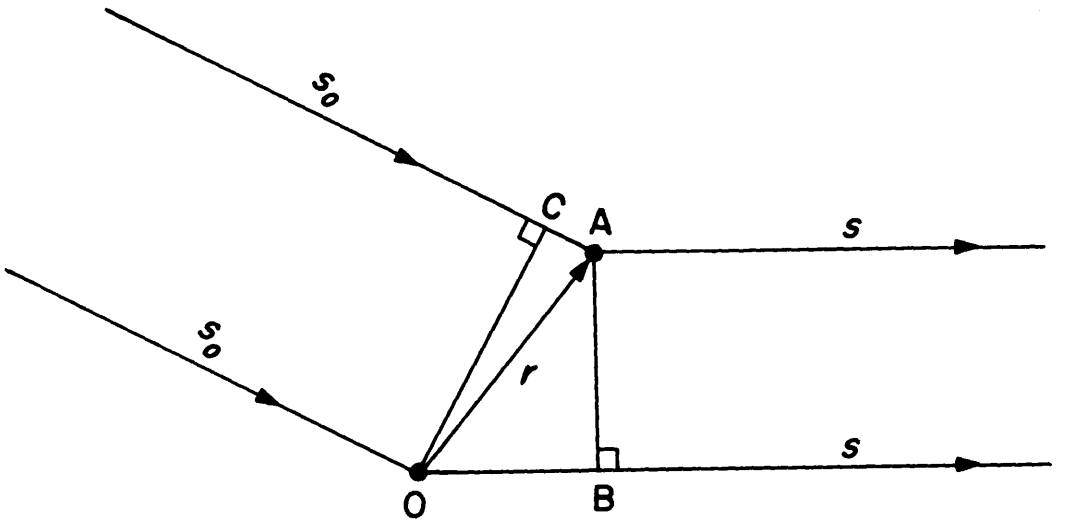


Fig. 1

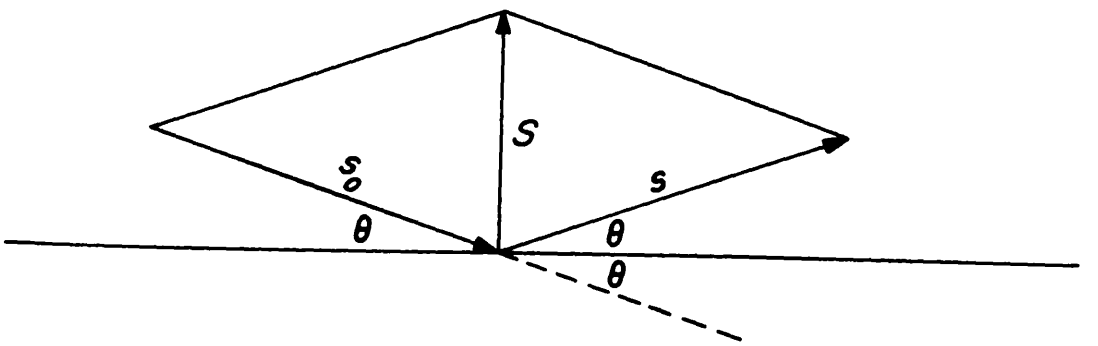


Fig. 2

waves. If n is an integer this condition can be written as

$$\lambda \underline{r} \cdot \underline{S} = \lambda \, (u\underline{a} + v\underline{b} + w\underline{c}) \cdot \underline{S} = n\lambda \tag{2}$$

For this to be valid for all values of u, v, and w we have to have

$$\begin{aligned} \underline{a} \cdot \underline{S} &= h \\ \underline{b} \cdot \underline{S} &= k \\ \underline{c} \cdot \underline{S} &= \ell \end{aligned} \tag{3}$$

where h, k, ℓ are integers. These are the Laue equations for constructive reinforcement of scattering by a lattice.

It was not possible to use Laue's equations for the determination of crystal structures until W. L. Bragg (1913) interpreted them in physical terms. By rewriting (3) to

$$\begin{aligned} &\underline{a}/h \cdot \underline{S} = \underline{b}/k \cdot \underline{S} = \underline{c}/\ell \cdot \underline{S} = 1 \\ \text{or} \quad &(\underline{a}/h - \underline{b}/k) \cdot \underline{S} = 0; \; (\underline{a}/h - \underline{c}/\ell) \cdot \underline{S} = 0, \text{ etc.} \end{aligned} \tag{4}$$

it can be seen that $\underline{S}$ is perpendicular to the plane of Miller indices hkℓ. By definition $\underline{a}/h$, $\underline{b}/k$, and $\underline{c}/\ell$ are the intercepts which this plane makes on the crystal axes. The spacing d of the hkℓ planes is the projection of either $\underline{a}/h$, $\underline{b}/k$, or $\underline{c}/\ell$ on the vector $\underline{S}$:

$$d = \frac{\underline{a}/h \cdot \underline{S}}{|\underline{S}|} \tag{5}$$

Assuming that the angle between the incident and diffracted beams is 2θ (Fig. 2) and inserting $\underline{a}/h \cdot \underline{S} = 1$ (eq. (4)), equation (5) can be rewritten as

$$d = \frac{\lambda}{2 \sin\theta} \tag{5a}$$

or

$$\lambda = 2 d \sin\theta$$

This is Bragg's law. The condition for constructive interference from a plane with Miller indices $hk\ell$ is, according to Bragg's law, analogous to the reflexion of light from a mirror.

As seen above, the diffraction vector $\underline{S}$ is normal to the crystal plane $hk\ell$ and its length is $1/d$ according to (5) and (5a).

In most aspects of X-ray diffraction the reciprocal lattice is of great importance. It can be defined by the non-coplanar axes $\underline{a}^*$, $\underline{b}^*$, and $\underline{c}^*$ by the conditions that

$$\underline{a} \cdot \underline{a}^* = 1 \tag{6}$$

and

$$\underline{b} \cdot \underline{a}^* = \underline{c} \cdot \underline{a}^* = 0 \tag{7}$$

Similar conditions apply to $\underline{b}^*$ and $\underline{c}^*$. The length of a reciprocal axis is, according to (6), inversely proportional to the magnitude of the corresponding real axis. From Laue's equations and the conditions (6) and (7) the

diffraction vector to the reciprocal lattice points can be written as:

$$\underline{S} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^* \tag{8}$$

Each reciprocal lattice point is uniquely defined by the three numbers h, k, and ℓ. The reciprocal axes can be expressed in terms of the crystal axes in real space. According to (7) $\underline{a}^*$ must be perpendicular to $\underline{b}$ and $\underline{c}$, hence

$$\underline{a}^* = K\, \underline{b} \times \underline{c} \tag{9}$$

Since $\underline{a} \cdot \underline{a}^* = 1$ equation (9) can be written:

$$\underline{a} \cdot (\underline{b} \times \underline{c})\, K = 1$$

or

$$K = \frac{1}{\underline{a} \cdot (\underline{b} \times \underline{c})} = \frac{1}{V} \tag{10}$$

where V is the volume of the unit cell. By inserting (10) in (9) the reciprocal axes are thus

$$\underline{a}^* = \frac{1}{V} (\underline{b} \times \underline{c})$$

$$\underline{b}^* = \frac{1}{V} (\underline{c} \times \underline{a}) \tag{11}$$

$$\underline{c}^* = \frac{1}{V} (\underline{a} \times \underline{b})$$

3. The structure factor

So far we have considered the scattering from a lattice with one electron at each lattice point. In reality the lattice consists of atoms and the electrons are distributed around the atomic nuclei. If $\rho_n(\underline{r})$ is the electron density at $\underline{r}$ of the n^{th} atom, the scattering by the entire atom can be written as

$$f_n(\underline{S}) = \int_{-\infty}^{+\infty} \rho_n(\underline{r}) \exp(2\pi i \underline{r}\cdot\underline{S})\, dV \qquad (12)$$

where $2\pi\underline{r}\cdot\underline{S}$ is the phase of a beam scattered at an angle θ from an electron at $\underline{r}$, relative to an origin chosen at the centre of the atom. The integral is over all the electrons; i.e. over the volume, V, of the atom. The quantity $f_n(\underline{S})$ is called the atomic scattering factor and is, according to (12), the Fourier transform of the atomic electron density. If the atom is centrosymmetric and the origin of $\underline{r}$ has been chosen at the centre of the atom, $f_n(\underline{S})$ is a real function. In this case $\rho_n(\underline{r})$ is spherically symmetric and thus a function of $|\underline{r}|$ only, and $f_n(\underline{S})$ a function of $|\underline{S}| = 2\sin\theta/\lambda$ only. The atomic scattering factor is the scattering power of a hypothetical particle at the atomic centre whose scattering power is equivalent to that of the collection of electrons associated with the

atom.

The electrons are distributed in space around the atomic nucleus and the mutual destructive interference of the scattered wavelets from each electron increases with increasing scattering angle, θ. Therefore the scattering power decreases with increasing values of θ. Approximate values of the scattering factors of atoms for X-rays can be obtained by theoretical calculations based on quantum theory. Results of such calculations for spherically symmetrical atoms are listed in International Tables for X-Ray Crystallography, Vol. III (1962).

A unit cell usually contains more than one atom. If it contains N atoms and $\underline{r}_n$ is the vector from the origin of the unit cell to the n^{th} atom, the scattering power of the unit cell can be written as

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp (2\pi i \underline{r}_n \cdot \underline{S}) \qquad (13)$$

Analogous to (1) the path difference of a ray scattered by the n^{th} atom relative to scattering by an atom at the origin is $\lambda \underline{r}_n \cdot \underline{S}$. This path difference corresponds to a phase difference of $2\pi \underline{r}_n \cdot \underline{S}$. $G(\underline{S})$ is a continuous function of θ and refers to the diffraction with scattering vector $\underline{S}$.

If the n^{th} atom has the fractional coordinates x_n, y_n,

and z_n with respect to the crystal axes, the vector $\underline{r}_n$ can be expressed as

$$\underline{r}_n = (x_n\underline{a} + y_n\underline{b} + z_n\underline{c}) \tag{14}$$

Substitution of (14) in (13) yields

$$G(\underline{S}) = \sum_{n=1}^{N} f_n(\underline{S}) \exp 2\pi i \, (x_n\underline{a}\cdot\underline{S} + y_n\underline{b}\cdot\underline{S} + z_n\underline{c}\cdot\underline{S}) \tag{15}$$

In a crystal there are many unit cells. Constructive interference of the scattered waves from the unit cells occurs only when the Laue conditions are obeyed, i.e. when $\underline{a}\cdot\underline{S} = h$; $\underline{b}\cdot\underline{S} = k$; and $\underline{c}\cdot\underline{S} = \ell$. Equation (15) can thus be written as

$$G(\underline{S}) = F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell) \exp 2\pi i \, (hx_n + ky_n + \ell z_n) \tag{16}$$

In the case of scattering from a crystal $G(\underline{S})$ is replaced by $F(hk\ell)$ which is called the structure factor. Equation (16) is the expression for the complete wave scattered by a unit cell in a crystal; but since all unit cells are scattering in phase it also describes the complete wave scattered by the whole crystal.

The structure factor is a function of h, k, and ℓ. In reciprocal space there is cancellation of the scattering due to destructive interference among unit cells, except

at the reciprocal lattice points hkℓ where, in general, scattering of waves with non-zero amplitudes occurs. F(hkℓ) is defined at these points only.

According to (16) the structure factor is complex and thus describes both the absolute value and the phase of the scattered wave. It can be written as:

$$F(hk\ell) = A + iB \tag{17}$$

and its conjugate

$$F^{*}(hk\ell) = F(\bar{h}\bar{k}\bar{\ell}) = A - iB \tag{18}$$

(assuming that Friedel's law, which states that $|F(hk\ell)| = |F(\bar{h}\bar{k}\bar{\ell})|$, holds) where

$$A = \sum_{n=1}^{N} f_n(hk\ell) \cos 2\pi (hx_n + ky_n + \ell z_n) \tag{19}$$

$$B = \sum_{n=1}^{N} f_n(hk\ell) \sin 2\pi (hx_n + ky_n + \ell z_n) \tag{20}$$

The modulus of F(hkℓ) is called the structure amplitude and can be expressed by

$$|F(hk\ell)| = (A^2 + B^2)^{\frac{1}{2}} \tag{21}$$

and its phase $\alpha(hk\ell)$ by

$$\tan \alpha(hk\ell) = B/A \tag{22}$$

In a centrosymmetric space group with the centre of symmetry at the origin, we have an atom at $(-x_n, -y_n, -z_n)$ for every atom at (x_n, y_n, z_n). Accordingly $B = 0$ (from (20)) and the phase is either 0° or 180°. The structure factor is then real.

If the positions of the atoms in the unit cell are known, the structure factors can be calculated directly by the above equations.

4. Thermal vibration

So far we have assumed that the atoms scattering X-rays are stationary. In fact, however, the atoms are oscillating and in a given crystal their oscillation increases with increasing temperature. This effect reduces the scattering factor of an atom by an amount which increases with increasing values of $\sin\theta/\lambda$. The scattering factor of an atom in thermal motion is the scattering factor of the atom at rest multiplied by the Fourier transform of the smearing function, $t(\underline{x})$. The smearing function is the probability for the centre of an atom to be displaced by $\underline{x}$ relative to the centre of the electron density. Bloch (1932) showed that this function is Gaussian for an atom vibrating in an isotropic harmonic potential field at a certain temperature. The transform of $t(\underline{x})$ is

$$q(\underline{S}) = \exp(-2\pi^2 U S^2) = \exp(-8\pi^2 U \sin^2\theta/\lambda^2) \qquad (23)$$

where $U = \overline{u^2}$ is the mean-square amplitude of vibration. The isotropic temperature factor is often expressed by the Debye-Waller factor, $B = 8\pi^2 U$.

Usually atoms vibrate anisotropically and the motion can then be described by a symmetrical tensor $\underline{U}$ with six independent components. In this case the mean-square amplitude of vibration in the direction of a unit vector $\underline{\ell} = (\ell_1, \ell_2, \ell_3)$ can be expressed by

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} \ell_i \ell_j \qquad (24)$$

$\underline{U}$ and $\underline{\ell}$ are referred to the reciprocal axes. The transform of the smearing function for anisotropic vibration at a reciprocal lattice point with the diffraction vector $\underline{S} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^*$ is

$$q(\underline{S}) = q(hk\ell) = \exp\{-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell hc^*a^* + 2U_{12}hka^*b^*)\} \qquad (25)$$

When thermal motion is considered the equation for the structure factor (16) can be written as

$$F(hk\ell) = \sum_{n=1}^{N} f_n(hk\ell)\, q_n(hk\ell) \exp 2\pi i (hx_n + ky_n + \ell z_n) \qquad (26)$$

5. Derivation of structure amplitudes from intensities

The absolute value of the structure factor $|F(hk\ell)|$ cannot be measured directly, but the related integrated intensity is observed.

Consider a very small crystal being rotated in such a way that a set of $hk\ell$ planes passes once through the reflecting position. The total energy of the reflected beam can then be expressed by the formula

$$E(hk\ell) = K \cdot L(hk\ell) \cdot p(hk\ell) \cdot |F(hk\ell)|^2 \tag{27}$$

where $$K = \left(\frac{I_o \lambda^3 N^2 \, dV}{\omega} \right) \left(\frac{e^4}{m^2 c^4} \right) \tag{28}$$

and is a constant for the experiment. The symbols in (28) are defined as follows:

I_o = the intensity of the incident beam
λ = the wavelength of the radiation
N = the number of unit cells per unit volume
dV = the volume of the crystal
ω = the angular velocity of the crystal
e = the charge of an electron
m = the mass of an electron
c = the velocity of light

Since the incident X-ray beam is not plane polarised,

it has to be corrected by the polarisation factor, $p(hk\ell) = \frac{1}{2}(1 + \cos^2 2\theta)$. The polarisation factor is a function of only the scattering angle 2θ and is thus independent of the method used for data collection. Its value ranges from $\frac{1}{2}$ to 1.

$L(hk\ell)$ is called the Lorentz factor and takes into account the fact that reciprocal lattice points pass through the sphere of reflexion at different speeds. The Lorentz factor varies with the method used for data collection. For equi-inclination Weissenberg geometry it has the form

$$L(hk\ell) = [\sin\theta(\cos^2\mu - \cos^2\theta)^{-\frac{1}{2}}] \cdot 1/\sin 2\theta \qquad (29)$$

The expression in the square brackets is the inverse of the rotation factor which was evaluated by Tunell (1939). The rotation factor is a correction for angular velocity of the upper layers relative to the zero layer. The angle μ is the equi-inclination angle.

The energies of the reflected beams can be measured by the blackening on photographic films or, more directly, by quantum counters. Equation (27) is valid only for integrated reflexions and preferably these should be measured instead of peak values.

The physical factors of absorption and extinction are more difficult to correct for than the above-mentioned

geometrical factors. They are negligible for a microscopic crystal only. They were not accounted for in equation (27) since the crystal considered had a very small volume, dV.

Absorption, the most important of the physical factors, occurs because part of the X-ray beam is absorbed by the crystal and consequently its intensity is reduced. This can be expressed by

$$I = I_o \exp(-\mu t) \tag{30}$$

where I_o is the intensity of the original beam and I its intensity after it has passed through a thickness t of the crystal. The linear absorption coefficient μ is a function of the material of the crystal and of the wavelength of X-rays employed. For spherical and cylindrical specimens reliable absorption corrections can be applied without too much trouble. However, for irregularly shaped crystals it is a complicated task.

Another physical phenomenon which results in attenuation of the incident beam, when the crystal is in diffracting position, is called extinction. It was dealt with by Darwin (1922), who divided it into primary and secondary extinction. X-rays which have already been reflected by a set of Bragg planes are at the correct angle for being reflected again by other planes of the same stack. Such

doubly-reflected rays are parallel to the incident beam. However, they are exactly out of phase and hence weaken it. This is primary extinction. For perfect crystals the intensity is reduced appreciably by this effect but since most crystals are mosaic the effect is usually small. The correction, which is difficult to make, is largest for low-order reflexions with large values of the structure factor. Primary extinction can sometimes be avoided by dipping the crystal into liquid air and hence making it mosaic.

Reflexion from a Bragg plane reduces the intensity of the incident beam. The intensity received by a lower plane is therefore equal to the intensity of the original beam less the reduction due to reflexion by the planes preceding it. This weakening of the intensity is called secondary extinction. It is also related to the mosaicity of the crystal and behaves similarly to ordinary absorption. It can be allowed for by increasing the value of the linear absorption coefficient.

The intensities of the reflexions are usually measured on an arbitrary scale. After these intensities have been corrected for Lorentz, polarisation, absorption, and extinction factors the observed structure factors, on an arbitrary scale, can be deduced from (27). These observed structure factors can be put on an absolute scale by

experimental comparison with a standard (Robertson, 1934). An alternative method is that of Wilson (1942). The curve obtained by plotting the logarithm of $\overline{|F_o|^2}/\overline{\Sigma f_n^2}$ as a function of $\sin^2\theta$ is a straight line. The absolute scale can be obtained from the intercept of the line with the ordinate axis and an overall isotropic temperature parameter from the slope. At a later stage of the structure analysis the absolute scale can be obtained by comparison of observed structure factors with those calculated from a reliable model of the structure. In the final stages it can be refined by least-squares methods.

6. The electron density

Since the structure of the crystal is periodic in three dimensions the electron density ρ at the point (xyz) can be expressed by a three-dimensional Fourier series. If h', k', and ℓ' are integers and x, y, and z fractional coordinates then

$$\rho(xyz) = \sum_{h'k'\ell'=-\infty}^{+\infty} \Sigma\Sigma\Sigma A(h'k'\ell') \exp\{-2\pi i (h'x + k'y + \ell'z)\} \qquad (31)$$

The structure factor is the Fourier transform of the electron density and can be expressed by

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 V\,\rho(xyz) \exp\{2\pi i (hx + ky + \ell z)\}\,dxdydz \qquad (32)$$

where $\rho V dxdydz$ is the amount of scattering matter in the volume element $Vdxdydz$. V is the volume of the unit cell. In order to determine the Fourier coefficient $A(h'k'\ell')$ the expression of the electron density (31) can be inserted in (32):

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 \sum_{h'}\sum_{k'}\sum_{\ell'}^{+\infty} A(h'k'\ell') \exp\{2\pi i[(h-h')x + (k-k')y + (\ell-\ell')z]\}Vdxdydz \tag{33}$$

The exponential function in (33) is periodical and its integral will therefore have a value only when $h = h'$, $k = k'$, and $\ell = \ell'$. The expression then becomes

$$F(hk\ell) = \int_0^1\int_0^1\int_0^1 A(hk\ell)Vdxdydz = A(hk\ell)\ V \tag{34}$$

$F(hk\ell)/V$ is hence the Fourier coefficient of the electron density which can now be expressed by

$$\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_{\ell}^{+\infty} F(hk\ell) \exp\{-2\pi i\ (hx + ky + \ell z)\} \tag{35}$$

Observed structure amplitudes, $|F_o|$, can be obtained from the observed intensities (equation (27)). However, since structure factors are complex quantities the electron density expressed by (35) cannot be evaluated without the knowledge of their phases. In order to solve a crystal

structure it is thus essential to know the phases of the structure factors. This is the phase problem in X-ray crystallography.

7. Methods of phase determination

(a) Patterson's vector synthesis

The following function, a convolution of the electron density ρ with itself, was defined by Patterson (1934 and 1935):

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\rho(x+u,\ y+v,\ z+w)\ dxdydz \qquad (36)$$

where V is the volume of the unit cell and u, v, and w are fractional coordinates. The product of the two electron densities in (36) has a value only when the vector with the components u, v, and w connects the electron density of one atom with that of another. Accordingly this function gives information about interatomic vectors. The electron density in (36) can be substituted by the expression (35) and we get:

$$P(uvw) = \frac{1}{V}\int_0^1\int_0^1\int_0^1 \sum_h\sum_k\sum_\ell\sum_{h'=-\infty}^{+\infty}\sum_{k'}\sum_{\ell'} F(hk\ell)\ \exp\{-2\pi i(hx+ky+\ell z)\}F(h'k'\ell')$$

$$\cdot\exp\{-2\pi i(h'x+k'y+\ell'z)\}\ \exp\{-2\pi i(h'u+k'v+\ell'w)\}dxdydz \qquad (37)$$

By applying the same reasoning as for equation (33) the

integral is zero unless $h = -h'$, $k = -k'$, and $\ell = -\ell'$. Since $F(hk\ell)$ and $F(\bar{h}\bar{k}\bar{\ell})$ are complex conjugates, i.e. $F(hk\ell)\cdot F(\bar{h}\bar{k}\bar{\ell}) = |F(hk\ell)|^2 = |F(\bar{h}\bar{k}\bar{\ell})|^2$, the Patterson function, or vector distribution, thus takes the form

$$P(uvw) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell}^{+\infty}_{-\infty} |F(hk\ell)|^2 \exp 2\pi i\,(hu + kv + \ell w) \qquad (38)$$

The summation in (38) can be grouped in pairs of $hk\ell$ and $\bar{h}\bar{k}\bar{\ell}$ and the Patterson function can be written as

$$P(uvw) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell}^{+\infty}_{-\infty} |F(hk\ell)|^2 \cos 2\pi\,(hu + kv + \ell w) \qquad (39)$$

The vector distribution of a structure is thus real and always centrosymmetric. It is a function of the modulus of the structure factors and can be obtained for all structures from the knowledge of observed intensities only. For a structure containing N atoms the Patterson function is composed of N(N-1) interatomic vectors. Very simple structures can be solved directly from the Patterson function. This becomes too difficult, however, when the structure is more complicated.

The relatively broad peaks of the Patterson synthesis can be made sharper and more pronounced by applying a sharpening or modifying function, M(S), to the observed structure factors. The interpretation of the Patterson

function can thus be facilitated. Since $S = 2 \sin\theta/\lambda$, $M(S)$ is a function of $\sin\theta/\lambda$. The sharpened structure factors can be expressed by $|F_M| = M(S) \cdot |F_o|$. A commonly used modifying function is $M(S) = 1/\hat{f}(S)$ where $\hat{f}(S)$ is the average of the atomic scattering factors scaled to unit scattering power. The sharpened structure factors then correspond to scattering from point atoms. For sharpening with respect to a particular type of atom, j, the above function takes the form $M(S) = Z_j/f_j(S)$, where Z_j is the number of electrons for that atom and $f_j(S)$ is its scattering factor. Since every atom has a thermal motion a sharpening function corresponding to a point atom at rest would be $M(S) = (Z_j/f_j(S)) \exp (B \sin^2\theta/\lambda^2)$, where B is the Debye-Waller temperature factor. The termination of the series at a finite number of terms will produce false detail in the background of a Patterson synthesis based on sharpened structure factors if the latter do not decline with $\sin\theta/\lambda$. This effect is greater for sharpening corresponding to point atom at rest than to point atom only.

Harker (1936) pointed out that useful information can be obtained from certain planes or lines of the three-dimensional Patterson function by making use of the space-group symmetry elements. If a two-fold screw axis parallel to the b-axis is considered, for instance, then there is

a peak of weight Z_j^2 in the Patterson function P(uvw) at $(2x_j, \frac{1}{2}, 2z_j)$ corresponding to a vector between the symmetry related atoms at (x_j, y_j, z_j) and $(\bar{x}_j, y_j + \frac{1}{2}, \bar{z}_j)$. The section through the Patterson function at $v = \frac{1}{2}$ is then called a Harker section.

(b) The heavy-atom method

If a structure contains a heavy atom (or a small number of them), the heavy atom can be used to determine the phases of the structure amplitudes. This so-called heavy-atom method is the most widely used one for solving crystal structures, especially moderately complicated ones. Usually the position of the heavy atom can be easily located from the three-dimensional Patterson function or from a Harker section. The phases based on the heavy atom alone can be calculated from its position. They are an approximation to the phases of the structure amplitudes and are in most cases sufficiently accurate for a subsequent determination of the structure.

The heavy-atom method is most successful when the ratio $r = (\Sigma_H f_H^2 / \Sigma_L f_L^2) \approx 1$, where H refers to the heavy atoms and L to the light ones. When $r = 1$ and the structure is non-centrosymmetric, about 40% of the reflexions will have errors smaller than 20° in their phases and 80%

will have errors smaller than 60° (Sim, 1961). If $r > 1$ the phases can be determined with greater accuracy, but it may not be possible to locate the lighter atoms, or at best, their positional coordinates will have low accuracy. The first direct application of the heavy-atom method was to the structure of platinum phthalocyanine by Robertson and Woodward (1940).

(c) The isomorphous-replacement method

The isomorphous-replacement method is more powerful than the heavy-atom method and has proved useful for several complicated organic structures, but its widest field of application has been in protein crystallography. The first successful use of this method was in the determination of the phthalocyanine structures (Robertson, 1935 and 1936; and Robertson and Woodward, 1937).

The fundamental equation of the isomorphous-replacement method in vector form is

$$\underline{F}_2 = \underline{F}_1 + \underline{f}_{12} \qquad (40)$$

where $\underline{F}_1$ and $\underline{F}_2$ are the structure factors of two isomorphous compounds and $\underline{f}_{12}$ is the calculated structure factor of the difference in scattering matter between structure 2 and structure 1. The vector $\underline{f}_{12}$ is completely known

while only the magnitudes of $\underline{F}_1$ and $\underline{F}_2$ are available. In the non-centrosymmetric case these two magnitudes can be used as radii of two circles whose centres are connected by the $\underline{f}_{12}$ vector. The two intersections of these circles, A and B, give the two possible solutions for the phase of $|F_1|$ (Bokhoven, Schoone, and Bijvoet, 1951). Figure 3 illustrates the two solutions. Each of them is equally probable, and Blow and Crick (1959) showed that the best result is obtained if the mid-point of the two is used. This is equivalent to applying the phase of $\underline{f}_{12}$ to the structure amplitude $|F_1|$ when $|F_2| < |F_1| + |f_{12}|$ and that of $-\underline{f}_{12}$ when $|F_1| < |F_2| + |f_{12}|$.

The ambiguity can be overcome by using another isomorphous derivative with a structure amplitude $|F_3|$. It is assumed that in this derivative an atom in a different position was replaced. For the third derivative the vector equation analogous to (40) is

$$\underline{F}_3 = \underline{F}_1 + \underline{f}_{13} \qquad (41)$$

The double isomorphous-replacement method was first suggested by Bokhoven *et al* (1951) and further developed by Harker (1956), who proposed its application to protein structures. If there are no errors in the structure amplitudes, the three circles representing the three

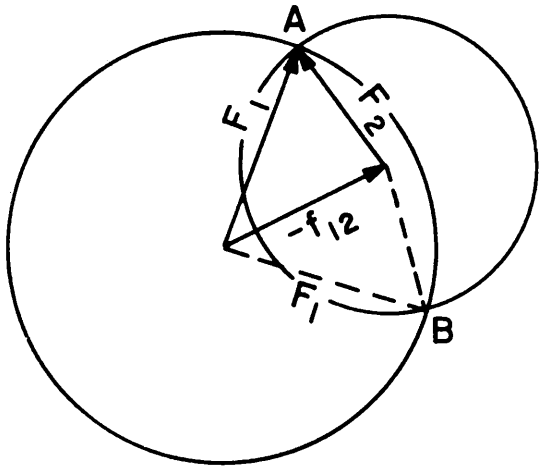


Fig. 3

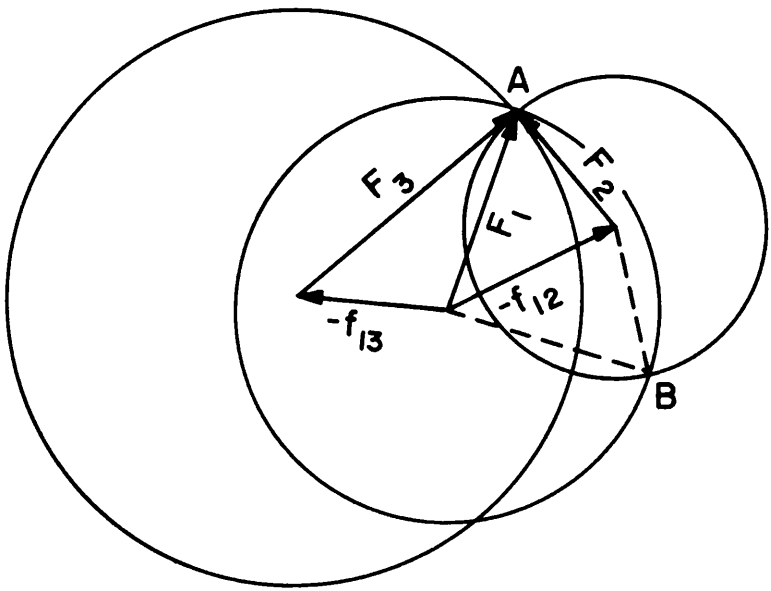


Fig. 4

structure amplitudes will intersect in one point, A, to give a unique solution to the phase of $|F_1|$ (Figure 4). In the case of proteins the errors associated with the structure amplitudes are considerable and it is therefore essential to use more than three isomorphous compounds in order to get reliable estimates of the phases.

After a structure has been solved, the refinement can be carried out on that isomorphous derivative which has the lightest atoms. In this way a higher accuracy can be obtained than by the heavy-atom method.

(d) Direct methods

The term "direct methods" usually means methods which involve certain mathematical relationships between structure factors for obtaining their phases. By the use of these methods there is no requirement for a heavy atom to be present and they have led to great progress in solving light-atom structures. They were first introduced by Harker and Kasper (1948) in the form of inequality relationships between structure factors. An important contribution to the development of direct methods was the equality relation between structure factors derived by Sayre (1952). This was further elaborated by Cochran (1952) and Zachariasen (1952) through the introduction of

a probability relationship. Karle and Hauptman (1953) described other probability relationships. These methods have been used mainly for centrosymmetric space groups. An example of a direct method applied to a non-centrosymmetric one is, for instance, the structure determination of the alkaloid panamin, $C_{20}H_{33}N_3$, (Karle and Karle, 1966a) by the symbolic addition procedure (Karle and Karle, 1966b).

8. Methods of refinement

After a preliminary model of the structure has been obtained, it is necessary to refine the postulated parameters in order to verify that the structure is correct and to obtain more accurate parameters. One way of expressing the reliability of a structure determination is by the residual or R-factor which is defined as

$$R = \sum_{hk\ell} \big| |F_o| - |F_c| \big| / \sum_{hk\ell} |F_o| \qquad (42)$$

where $|F_o|$ is the observed structure amplitude and $|F_c|$ is the one calculated for the model. The summations are over all the reflexions used in the refinement. Correct structures usually have an R-factor less than 25%.

(a) Successive Fourier syntheses

This method is usually applied in the early stage of

refinement when perhaps only part of the structure is known. When atomic positions are being improved or new atoms are being located from an electron-density distribution, the phases calculated from the new model will come closer to the correct values. By using these phases in a subsequent electron-density calculation new adjustments in the parameters become possible. Before all the atoms have been located it is useful to apply weighting functions to the Fourier terms and thus improve the electron density map (Woolfson, 1956; and Sim, 1961).

For a non-centrosymmetric structure it can be shown that a Fourier synthesis based on structure amplitudes of the correct structure and the phase angles of a postulated one, yields an electron-density map corresponding approximately to the average of the two structures. Convergence is therefore achieved more rapidly if a shift twice the observed one is applied. The Fourier refinement terminates when no new adjustments in the parameters can be made.

Since an infinite number of terms are not used in the electron-density Fourier series, the latter contains errors due to termination of series. Corrections of atomic parameters derived from an F_o synthesis can be made by the method of Booth (1946, 1947). In a Fourier synthesis based on calculated structure factors, the F_c synthesis,

the same errors will be produced. Consequently the atomic positions resulting from an F_c synthesis will not be the same as those used for its calculation. These shifts, with opposite sign, can be applied to the parameters derived from the F_o synthesis. The corrections for termination of series are unnecessary when a structure is later refined by the method of least squares.

(b) The difference Fourier synthesis

The difference between the electron density based on observed structure factors and one based on calculated ones is called the difference synthesis. The expression for it is

$$D = \rho_o - \rho_c = \frac{1}{V} \sum_{hk\ell} (F_o - F_c) \exp \{-2\pi i (hx + ky + \ell z)\} \quad (43)$$

It is a Fourier series with $(F_o - F_c)$ as coefficients and was suggested by Booth (1948a) as a method of refinement. Cochran (1951) showed that the function

$$\phi_j = \sum_{hk\ell} \frac{1}{f_j} (F_o - F_c)^2 \quad (44)$$

has a minimum with respect to the coordinates x_j, y_j, z_j of the j^{th} atom when the difference map has zero slope at the centre of this atom, i.e. when

$$\frac{\partial D}{\partial x_j} = \frac{\partial D}{\partial y_j} = \frac{\partial D}{\partial z_j} = 0 \quad (45)$$

The difference map for a completely refined structure is thus essentially flat with only random fluctuations due to experimental errors.

An error in the position of an atom results in a gradient in the difference map at the location of this atom. The correction for this error, in Å, is

$$\partial r_j = \frac{\partial D}{\partial r_j} \; / \; 2p(\rho_o)_j \qquad (46)$$

where $\frac{\partial D}{\partial r_j}$ is the gradient at the atom j in the gradient's steepest direction r, $(\rho_o)_j$ is the maximum electron density of the atom and p is the curvature of the peak.

The difference map will also indicate errors in temperature parameters. If an atom vibrates isotropically, a single peak in the difference map at the position of this atom indicates that the temperature factor applied in the calculation of F_c's was too large. If an atom is assumed to vibrate isotropically, while in fact it vibrates anisotropically, this results in characteristic peaks and valleys in the difference map and appropriate corrections can be applied (Cruickshank, 1956a).

In present-day crystallography the difference synthesis is used mainly for the location of hydrogen atoms and as a check of the results after the least-squares refinement.

(c) Least-squares refinement

A crystal structure can be refined by the method of least squares when a function of the difference between the observed and calculated structure factors is minimised with respect to the structural parameters. The function most commonly used is

$$M = \sum_{hk\ell} w \left(|F_o| - |F_c|\right)^2 \qquad (47)$$

The summation is over all structure amplitudes from independent observations and w is the weight of each term. The value of w which will give the lowest standard deviations for the parameters refined is $w(hk\ell) = {}^{1}/\sigma^2(hk\ell)$, where $\sigma^2(hk\ell)$ is the estimated variance of $|F_o(hk\ell)|$ due to random experimental errors. Generally it is more practicable to use weights which reflect trends in the $|\Delta| = \big||F_o| - |F_c|\big|$. For photographic data a weighting scheme of the form $w = (p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{-1}$ (Cruickshank, Pilling, Bujosa, Lovell, and Truter, 1961) has often been useful. If the "best" weighting scheme has been used, the averages of $w\Delta^2$ should be close to constant when they are analysed as a function of increasing $|F_o|$ or of increasing $\sin\theta/\lambda$ values.

Comparison of equations (47) and (44) shows that refinement by difference synthesis is related to the one by

least squares in which the weights were chosen to be $1/f_j$.

In order to determine the parameters $p_1, p_2, \ldots p_n$ which are being refined and which will minimise M the condition

$$\partial M/\partial p_j = 0 \qquad (j=1, 2, \ldots n) \tag{48}$$

must hold. By applying this condition to (47) one obtains

$$\sum_{hk\ell} w\Delta \frac{\partial |F_c|}{\partial p_j} = 0 \qquad (j=1, 2, \ldots n) \tag{49}$$

where $\Delta = |F_o| - |F_c|$. If the values of p_j are close to their true values, Δ may be expanded as a function of the parameters by a Taylor series of the first order

$$\Delta(\underline{p} + \underline{\varepsilon}) = \Delta(\underline{p}) - \sum_{i=1}^{n} \varepsilon_i \frac{\partial |F_c|}{\partial p_i} \tag{50}$$

where $\underline{p}$ and $\underline{\varepsilon}$ stand for a whole set of parameters and changes and ε_i is a small change in a parameter p_i. By substituting Δ from (50) in (49) one gets

$$\sum_{i=1}^{n} \left(\sum_{hk\ell} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \right) \varepsilon_i = \sum_{hk\ell} w\Delta \frac{\partial |F_c|}{\partial p_j} \qquad (j=1, 2, \ldots n) \tag{51}$$

These n equations are called the normal equations and can also be expressed in matrix form as

$$\sum_{i} a_{ij} \varepsilon_i = b_j \qquad (j=1, 2, \ldots n) \tag{52}$$

where $$a_{ij} = \sum_{hk\ell} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \tag{53}$$

and $$b_j = \sum_{hk\ell} w\Delta \frac{\partial |F_c|}{\partial p_j} \tag{54}$$

The normal equations have to be solved in order to determine the n unknowns and thus refine a structure. The n solutions are

$$\varepsilon_j = \sum_{i=1}^{n} (a^{-1})_{ij} b_i \qquad (j=1, 2, \ldots n) \tag{55}$$

where $\underline{a}^{-1}$ is the inverse matrix of $\underline{a}$.

Before the normal equations are solved, $\partial |F_c|/\partial p_j$ has to be evaluated for each of the parameters refined. If α is the phase of the calculated structure factor, $|F_c|$ can be written as

$$|F_c| = A \cos \alpha + B \sin \alpha \tag{56}$$

where $$A = \sum_r \sum_s A_{rs} = \sum_r A_r \tag{57}$$

and $$B = \sum_r \sum_s B_{rs} = \sum_r B_r \tag{58}$$

A_{rs} is the contribution from one atom s related to atom r by symmetry and A_r is the contribution from atom r and its symmetry equivalents. B_{rs} and B_r are defined similarly.

If p_j is a parameter of atom r and its equivalents, it can be shown that

$$\frac{\partial |F_c|}{\partial p_j} = \frac{\partial A_r}{\partial p_j} \cos \alpha + \frac{\partial B_r}{\partial p_j} \sin \alpha \tag{59}$$

If anisotropic vibration is considered and an overall scale factor G is applied to $|F_c|$, we can write

$$A_{rs} = G f_{rs} \exp \{-2\pi^2 (U_{11,rs}h^2a^{*2} + U_{22,rs}k^2b^{*2} + \ldots)\} \cdot \cos 2\pi (hx_{rs} + ky_{rs} + \ell z_{rs}) \tag{60}$$

and

$$B_{rs} = G f_{rs} \exp \{-2\pi^2 (U_{11,rs}h^2a^{*2} + U_{22,rs}k^2b^{*2} + \ldots)\} \cdot \sin 2\pi (hx_{rs} + ky_{rs} + \ell z_{rs}) \tag{61}$$

By substituting (60) and (61) in (59) $\partial |F_c| / \partial p_j$ can thus be evaluated for all the p_j parameters.

The scale factor G is the only parameter which is a linear function of $|F_c|$. For the other parameters the assumption that the second and higher order terms of the Taylor series are so small that they can be ignored in equation (50) leads to solutions of the normal equations which do not give the true minimum of M. Several successive cycles of refinement are therefore usually necessary.

The scale factor G derived from a least-squares cycle applies to $|F_c|$. However, it is the $|F_o|$'s which we want to put on an absolute scale. This is done after each cycle of refinement by applying the scale factor $K = {}^1/G$ to them.

When layer-scale factors are refined, each $|F_o|$ may be observed on one or more "layer lines". The data have to be arranged in batches, i, and all the reflexions in each batch will have the same scale factor, G_i. The G_i layer-scale factor also applies to $|F_c|$ and after each cycle of refinement the inverse scale factor $K_i = {}^1/G_i$ is applied to $|F_o|_i$.

The number of independent elements in the matrix $\underline{a}$ of equation (52) is $n(n+1)/2$ where n is the number of parameters refined. Due to limitations in storage capacity of electronic computers, the full-matrix least squares can only be used for small molecules. For medium and large molecules approximations have to be applied where many of the off-diagonal elements a_{ij} $(i \neq j)$ in the matrix $\underline{a}$ are neglected.

The block-diagonal approximation of the least-squares programme written by Cruickshank and Smith for the Glasgow KDF 9 computer uses a chain of 9 × 9 matrices for the refinement of fractional coordinates and the anisotropic temperature parameters of each atom as well as a $(n+1) \times (n+1)$

matrix for the n layer-scale factors and overall isotropic temperature-factor refinement. For isotropic vibration a 4×4 matrix is calculated for each atom.

Convergence is reached more slowly when the block-diagonal approximation is used. The process can be accelerated if the shifts obtained from the least-squares equations are reduced by a partial shift, or "fudge" factor. A value of 0.8 for the partial-shift factor has frequently been used.

The course of the refinement can be followed by inspecting the change of $M = \sum_{hk\ell} w\Delta^2$, or better by the change of $R' = \sum_{hk\ell} w\Delta^2 / \sum_{hk\ell} w F_o^2$.

9. Accuracy and analysis of results

Estimated standard deviations of the parameters refined by least squares can easily be evaluated in the course of the refinement. For full-matrix least squares using relative weights which reflect the trend in $|\Delta F|$, the estimated variance of a parameter is

$$\sigma^2(p_i) = (a^{-1})_{ii} \left(\sum_{hk\ell} w\Delta^2 \right)/(m-n) \qquad (62)$$

where $(a^{-1})_{ii}$ is an element of the matrix inverse to $\underline{a}$, m is the number of observations, and n is the number of

parameters refined. In the block-diagonal refinement the inverse of the block matrices is used in (62). The covariance of the parameters p_i and p_j can be estimated from

$$\begin{aligned} \text{cov}\ (p_i p_j) &= (a^{-1})_{ij} \left(\sum_{hk\ell} w\Delta^2 \right)/(m-n) \\ &= \sigma(p_i)\ \sigma(p_j)\ r_{ij} \end{aligned} \tag{63}$$

where r_{ij} is the correlation coefficient of the parameters.

The standard deviation of a bond length ℓ_{12}, when there is no correlation between the coordinates of the two atoms, is

$$\sigma(\ell_{12}) = (\sigma^2(x_1) + \sigma^2(x_2))^{\frac{1}{2}} \tag{64}$$

where $\sigma(x_1)$ and $\sigma(x_2)$ are the standard deviations of the atomic coordinates in the direction of the bond. Applying the same condition as for equation (64), the standard deviation in the angle β between the bonds ℓ_{12} and ℓ_{23} is

$$\sigma(\beta) = \left(\frac{\sigma^2(x_1)}{\ell_{12}^2} + \frac{\ell_{13}^2}{\ell_{12}^2 \ell_{23}^2}\, \sigma^2(x_2) + \frac{\sigma^2(x_3)}{\ell_{23}^2} \right)^{\frac{1}{2}} \tag{65}$$

where $\sigma(x_1)$ and $\sigma(x_3)$ are the coordinate standard deviations of atoms 1 and 3 in the directions at right angles to ℓ_{12} and ℓ_{23}, respectively, and $\sigma(x_2)$ is the coordinate standard deviation of atom 2 in the direction of the centre

of the circle passing through the three atoms (Darlow, 1960).

Before drawing conclusions from a comparison of a bond length or bond angle with a theoretical value or from comparison of two different experimental determinations, it is necessary to use statistical significance tests based on proper estimates of the accuracy of the results (Cruickshank and Robertson, 1953). If ℓ_o, with estimated standard deviation s_o, is the experimental estimate of an unknown quantity whose true value is λ_o, then

$$t_o = (\ell_o - \lambda_o)/s_o \qquad (66)$$

is a value of a random variable t having the Student's probability distribution with ν degrees of freedom (ν is the difference between the number of independently observed reflexions and the independent parameters derived from the data). In a three-dimensional analysis ν is usually so large that it can be set at ∞. Fisher and Yates (1953) list the probabilities P that $|t| \geq |t_o|$ for various values of t_o, e.g.

P = 5%	t_o = 2.0
P = 1%	t_o = 2.6
P = 0.1%	t_o = 3.3

Results are referred to as being significant at a 5%, 1%, or 0.1% level.

If a least-squares plane through a set of n points is considered and d_i is the deviation of the i^{th} point from that plane and σ_i the average positional standard deviation of a point, then the function

$$\chi^2 = \sum_{i=1}^{n} (d_i^2/\sigma_i^2) \tag{67}$$

has a χ^2 probability distribution with (n-3) degrees of freedom. The probability that the deviations from the plane are due to random experimental errors can be found by applying the χ^2 significance test using for instance the tables of Fisher and Yates (1953).

10. Anomalous dispersion

If a scattering atom has an absorption edge close to the radiation wavelength and on the long side of it, the scattered wave has a relatively large anomalous phase shift. The atomic scattering factor can in this case be written as

$$f = f_o + \Delta f' + i\Delta f'' \tag{68}$$

where $\Delta f'$ and $\Delta f''$ are, respectively, the real and imaginary corrections for anomalous scattering. In non-centrosymmetric

space groups Friedel's law, $|F(hk\ell)| = |F(\bar{h}\bar{k}\bar{\ell})|$, is therefore no longer valid. (In centrosymmetric space groups it is always valid because of symmetry.) If A and B are defined by equations (19) and (20) and $f_n = (f_o)_n + \Delta f_n'$ is the real part of the atomic scattering factor, then

$$\begin{aligned} F(hk\ell) &= (A + i\Delta A) + i\,(B + i\Delta B) \\ &= (A - \Delta B) + i\,(B + \Delta A) \end{aligned} \tag{69}$$

and $$F(\bar{h}\bar{k}\bar{\ell}) = (A + \Delta B) + i\,(-B + \Delta A) \tag{70}$$

where $$\Delta A = \sum_{n=1}^{N} \Delta f_n'' \cos 2\pi\,(hx_n + ky_n + \ell z_n) \tag{71}$$

and $$\Delta B = \sum_{n=1}^{N} \Delta f_n'' \sin 2\pi\,(hx_n + ky_n + \ell z_n) \tag{72}$$

From equations (69) and (70) it follows that $|F(hk\ell)| \neq |F(\bar{h}\bar{k}\bar{\ell})|$ or $|F(hk\ell)|^2 \neq |F(\bar{h}\bar{k}\bar{\ell})|^2$. Anomalous scattering results in differences in the intensities of the $hk\ell$ and $\bar{h}\bar{k}\bar{\ell}$ pairs of reflexions. Bijvoet (1949) pointed out that these differences can be used to determine the absolute configuration of molecules, i.e. to distinguish optical isomers. The effect of anomalous scattering is much smaller when the wavelength of the incident beam is quite far away from the absorption edge of the scattering atom, but it may still be appreciable, as in the case of bromine

with CuKα radiation.

In order to establish the absolute configuration it is essential to hold strictly to one coordinate system, e.g. a right-handed one, and to index the reflexions accordingly (Peerdeman and Bijvoet, 1956).

As pointed out by Ueki, Zalkin, and Templeton (1966) and dealt with in more detail by Cruickshank and McDonald (1967), an error is introduced in a particular coordinate of each anomalously scattering atom in a polar space group if correction for $\Delta f''$ is neglected. In space group $P2_1$, for instance, this will happen if reflexions are measured only from one-half of the accessible volume of reciprocal space (e.g. with k only positive). In this space group, if a bromine atom is the anomalous scatterer, its y coordinate will have a "polar dispersion" error.

As previously mentioned, the single isomorphous-replacement method for a non-centrosymmetric space group leads to an ambiguity in the determination of phase angles. The ambiguity can be resolved if the replaceable atom in one of the isomorphous structures scatters anomalously (Bijvoet, 1954). The combination of isomorphous replacement and anomalous scattering has been particularly useful in protein structure determinations (Kartha and Parthasarathy, 1965; and Matthews, 1966).

11. Rigid-body thermal vibration

The anisotropic thermal motion of certain molecules can be described in terms of rigid-body vibration. In these molecules the internal vibrations (stretching and bending of bonds) are much smaller than their rigid-body vibration. The mean-square displacement resulting from anisotropic rigid-body vibration of a molecule can be expressed, as an approximation, in terms of two symmetric tensors, $\underline{T}$ and $\underline{\omega}$, each with six independent components (Cruickshank, 1956b). The tensor $\underline{T}$ gives the translational vibrations of the mass centre in $\mathring{A}^2$ and the tensor $\underline{\omega}$ gives the angular oscillations (or librations) about the mass centre in (radians)^2. The mean-square amplitude for rigid-body vibration, $\overline{u^2}$, of the r^{th} atom in the molecule in the direction $\underline{\ell}$ can be expressed as

$$\overline{u^2} = \sum_{i=1}^{3}\sum_{j=1}^{3} U^r_{ij}\ell_i\ell_j = \sum_{i=1}^{3}\sum_{j=1}^{3} T_{ij}\ell_i\ell_j + \sum_{i=1}^{3}\sum_{j=1}^{3} \omega_{ij}\,(\underline{\ell} \times \underline{X}_r)_i(\underline{\ell} \times \underline{X}_r)_j \qquad (73)$$

It is assumed here that the atomic coordinates $\underline{X}_r = (X_r, Y_r, Z_r)$ and the vibration tensors $\underline{U}^r$ are referred to orthogonal axes with origin at the centre of mass. If

there are N atoms in the molecule there are N $\underline{U}^r$-tensors, i.e. N equations like (73). In the general case six linear observational equations are obtained for each atom by equating coefficients of $\ell_i \ell_j$ in (73). The typical equations are

$$\begin{aligned} U_{11} &= T_{11} + Z^2\omega_{22} + Y^2\omega_{33} - 2YZ\omega_{23} \\ U_{12} &= T_{12} - XY\omega_{33} - Z^2\omega_{12} + XZ\omega_{23} + YZ\omega_{13} \end{aligned} \qquad (74)$$

The 12 independent elements of $\underline{T}$ and $\underline{\omega}$ can be determined by least-squares procedures by minimising the function

$$M = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{r=1}^{N} w_{ij}^r \left(U_{ij,obs}^r - U_{ij,calc}^r\right)^2 \qquad (75)$$

where w is the weight. $U_{ij,calc}^r$ is calculated from (74), and the observed U_{ij}^r refers to the same orthogonal axes as the calculated one. The anisotropic thermal parameters, referred to reciprocal axes and given by (25), can be transformed first to the standard orthogonal axes, if necessary, and then to the orthogonal inertial axes, as described by Cruickshank *et al* (1961).

The effect of a librational motion of a molecule is to make all atoms appear closer to the axis about which libration occurs. This effect can be corrected if the thermal motion of a molecule has been successfully interpreted

in terms of the $\underline{T}$ and $\underline{\omega}$ tensors. According to Cruickshank (1961a) the corrections for librational motion to the coordinates X, Y, and Z are

$$\begin{aligned} \Delta_X &= \tfrac{1}{2}\,(X(B_{22} + B_{33}) - YB_{12} - ZB_{13}) \\ \Delta_Y &= \tfrac{1}{2}\,(Y(B_{33} + B_{11}) - ZB_{23} - XB_{12}) \\ \Delta_Z &= \tfrac{1}{2}\,(Z(B_{11} + B_{22}) - XB_{13} - YB_{23}) \end{aligned} \tag{76}$$

where $\underline{B} = \underline{A}^{-1}$ and $\underline{A}$ is a third-order symmetric matrix whose typical elements are

$$\begin{aligned} A_{11} &= (Y^2 + Z^2)/q^2 + \omega_{11}^{-1} \\ A_{12} &= -XY/q^2 + \omega_{12}^{-1} \end{aligned} \tag{77}$$

The shape of the atomic electron-density peak is assumed to be Gaussian before rotational oscillation is considered and q^2 is the breadth parameter for the peak.

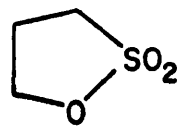
PART II

CHAPTER I

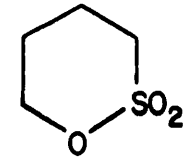
The Crystal Structure of 2-(o-Hydroxyphenyl)-1-phenyl-propanesulphonic Acid Sultone (Sultone B).

1. Introduction

Intramolecular esters of hydroxysulphonic acids are called sultones. Most of them have five- or six-membered rings (I, II) and the rings can be either saturated or



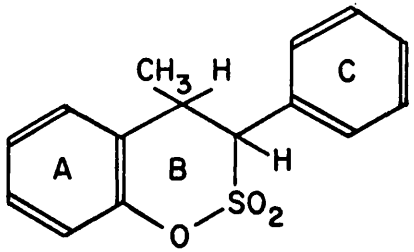
I



II

unsaturated. Sultones are very reactive alkylating reagents and they are useful for making organic substances water-soluble by adding the SO_3^- group (Helberger, Manecke, and Heyden, 1949). This finds practical application in the syntheses of detergents, dyestuffs, etc. Structural determinations of sultones by degradative methods are occasionally difficult and Ohline, Allred, and Bordwell (1964) have used proton magnetic resonance spectroscopy for such investigations. However, no X-ray investigation of a sultone had been carried out at the time when this work was started.

The synthesis of 2-(o-hydroxyphenyl)-1-phenylpropane-sulphonic acid sultone (III) by Timoney and co-workers (1966) yielded equal amounts of two isomers; one with m.p. 106°-108°C (sultone B) and the other with m.p. 158-160°C (sultone C). (Some earlier work on these sultones is described by Philbin, Stuart, Timoney, and Wheeler (1956)).



III

The former is converted entirely to sultone C when it is heated under reflux with 10% sodium hydroxide. Timoney suggested that in one of the isomers the methyl group is *cis* to the phenyl group and that in the second isomer they are *trans* to each other. It was not possible to distinguish these chemically. The crystals of sultone B are monoclinic while those of sultone C are triclinic, and the former were chosen for the crystal structure analysis in order to determine the configuration and accurate dimensions of the molecule.

2. Crystal data

2-(o-Hydroxyphenyl)-1-phenylpropanesulphonic acid sultone

(sultone B), $C_{15}H_{14}O_3S$, F.W. = 274.3, m.p. = 106°-108°C. Monoclinic, a = 11.18 ± 0.01, b = 10.70 ± 0.01, c = 14.42 ± 0.01 Å, β = 129.6 ± 0.2°. V = 1329.0 Å^3. D_m = 1.374 g.cm.$^{-3}$ (by flotation in a mixture of o-bromotoluene (D = 1.42 g.cm.$^{-3}$) and ethylbenzoate (D = 1.04 g.cm.$^{-3}$)), Z = 4, D_x = 1.371 g.cm.$^{-3}$. F(000) = 576. Space group P $2_1/c$ (No. 14) from systematic absences. Linear absorption coefficient μ = 21.1 cm.$^{-1}$ for Cu Kα radiation (λ = 1.5418 Å).

3. Crystallographic measurements

The crystals of sultone B are colourless and stable in the air as well as in the X-ray beam. They are elongated prisms with the c-axis parallel to the elongation.

Oscillation and Weissenberg photographs were taken with Cu Kα (λ = 1.5418 Å) radiation from crystals mounted along the c- and b-axes. The unit-cell parameters were measured from oscillation and zero-layer Weissenberg photographs. The standard deviations given for the cell dimensions are the root-mean-square deviations obtained from the individual measurements. The space group was determined uniquely from systematic absences (0k0 absent if k is odd, h0ℓ absent if ℓ is odd).

The three-dimensional intensity data were obtained

from a non-integrating equi-inclination Weissenberg camera using the multiple-film technique (Robertson, 1943). The crystal used was cut to a size of 0.25 × 0.35 × 0.60 mm. It was mounted along the longest direction which corresponded to the b-axis. The reciprocal lattice nets h0ℓ - h9ℓ were thus obtained. The intensities of the reflexions were measured visually by comparison with a calibrated intensity strip and 2,063 reflexions (72% of the 2,872 reflexions accessible within the copper sphere) were observed. The reflexions with intensities too low to be measured were not included in any of the calculations.

The intensities were corrected for absorption, assuming a cylindrical specimen with a diameter of 0.3 mm ($\mu R = 0.317$) and for Lorentz and polarisation factors. Initially the data were put on a common scale by ensuring that $\sum_{hk\ell} k|F_o| = \sum_{hk\ell} |F_c|$ for each layer. The layer scale factors were later refined by least-squares methods.

4. Structure determination

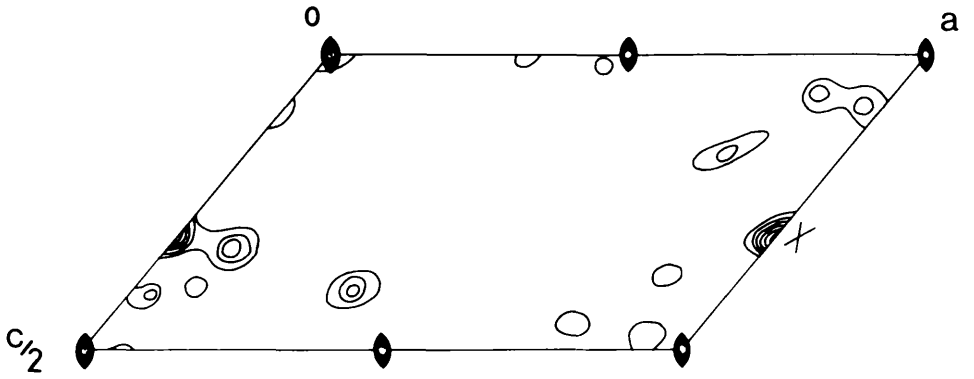
The heavy-atom technique was used in solving this structure even though the ratio $\Sigma f_H^2/\Sigma f_L^2$ has the low value of 0.34 at $\sin\theta/\lambda = 0$. During the structure determination and the Fourier refinement only data from seven layers (1586 reflexions) were used. The 477 reflexions from the

last three layers were added at the beginning of the least-squares refinement.

For space group P $2_1/c$ the symmetry of the Patterson vector distribution is P 2/m. The four equivalent positions in P $2_1/c$ are (x,y,z), $(\bar{x},\bar{y},\bar{z})$, $(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$, and $(x,\frac{1}{2}-y,\frac{1}{2}+z)$ and hence symmetry-related atoms will yield vector peaks at $(2x,\frac{1}{2},2z-\frac{1}{2})$, $(0,2y-\frac{1}{2},\frac{1}{2})$, and $(2x,2y,2z)$ in the Patterson map. The first two will have double weight but the last will be single-weighted. A three-dimensional Patterson synthesis was computed with the data sharpened to point atom at rest with respect to the sulphur atom. A $B = 4.0$ was used in the sharpening function, $M = \frac{Z}{f} \exp(B \sin^2\theta/\lambda^2)$. Figure 1.1 shows the Harker section at $v = \frac{1}{2}$ and a section at $w = \frac{1}{2}$. The latter contains the Harker line at $u = 0$, $w = \frac{1}{2}$. The highest peak in the Harker section and on the Harker line is marked with a cross. The two peaks have approximately equal heights and were assumed to arise from the sulphur-sulphur vector peaks $(2x,\frac{1}{2},2z-\frac{1}{2})$ and $(0,2y-\frac{1}{2},\frac{1}{2})$. The fractional coordinates of the sulphur atom were deduced from these two peaks by Booth's (1948b) method of interpolation: $x = 0.4988$, $y = 0.2962$, and $z = 0.4049$. Corresponding to these coordinates a peak at $(2x,2y,2z)$ in the Patterson map was observed. It had the correct peak height for being the

Figure 1.1

Sections through the three-dimensional Patterson synthesis (based on sharpened data to point atom at rest for the sulphur atom) at $v = \frac{1}{2}$ and at $w = \frac{1}{2}$. Contours are at arbitrary intervals.


o
a
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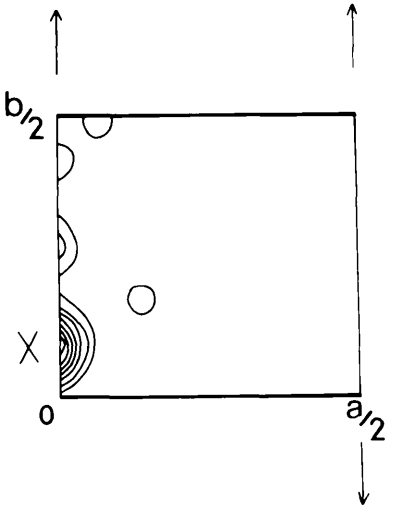
X


b/2
X
o
a/2

third sulphur-sulphur vector, namely close to half of that for the two other peaks. No attempt was made to deduce the position of any other atom from the Patterson synthesis.

A structure-factor calculation with the sulphur atom in the above-mentioned position resulted in an R-factor of 66%. From the first electron-density map, based on observed structure amplitudes and calculated phases from the sulphur position, the three oxygen atoms as well as eight carbon atoms were located. Inclusion of these atoms in the following structure-factor calculation lowered R to 49%. From the subsequent Fourier summation the remaining seven carbon atoms were found and with all the atoms included the R-factor fell to 30%. Improved coordinates were obtained from another Fourier synthesis and reduced R to 25.5%. In the structure-factor calculations an overall isotropic temperature parameter of B = 4.0 was used and the values for the atomic scattering factors were taken from International Tables for X-Ray Crystallography (1962).

5. Structure refinement

The positional and thermal parameters of the atoms and the individual layer-scale factors were refined by least-squares methods minimising the function $\sum_{hk\ell} w(|F_o| - |F_c|)^2$. The weighting scheme employed was

of the form recommended by Cruickshank *et al* (1961) for photographic data

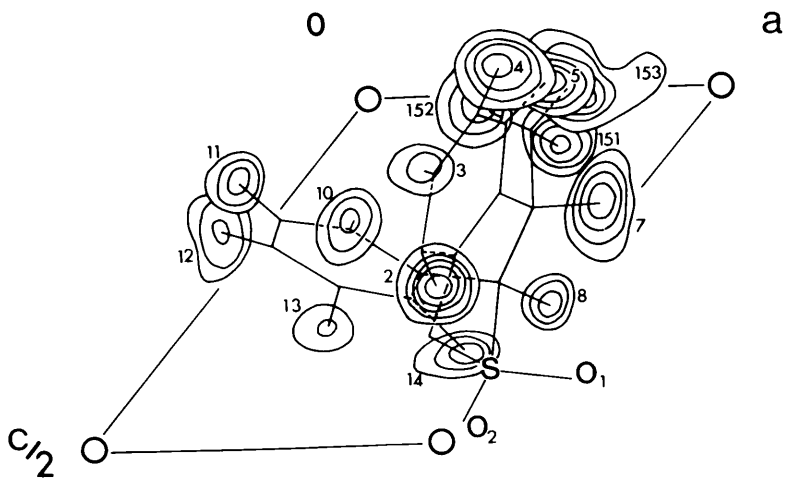
$$w = 1/(2.4 + |F_o| + 0.017|F_o|^2 + 0.00038|F_o|^3)$$

In an early stage of the refinement the $|F_o|^3$ term was omitted.

Four cycles of full-matrix isotropic refinement led to convergence, the value of R being 21.3%. Anisotropic temperature parameters were then introduced and after three cycles of block-diagonal refinement, the R-factor was reduced to 11.8%. At this point corrections for anomalous dispersion were introduced. The real and imaginary parts of these corrections are: $\Delta f' = 0.3$, $\Delta f'' = 0.6$ for sulphur and $\Delta f' = 0.0$, $\Delta f'' = 0.1$ for oxygen. Further refinement applying these terms reduced R to 11.7%. A difference Fourier synthesis computed at this point of the refinement, revealed all the hydrogen atoms with peak heights ranging from 0.30 to 0.75 $e\text{Å}^{-3}$. Figure 1.2 shows the hydrogen peaks in the composite three-dimensional Fourier map viewed down the b-axis. The hydrogen atoms are numbered according to the carbon atoms to which they are bonded. A further six cycles of block-diagonal least-squares refinement in which the non-hydrogen atoms were refined anisotropically and the

Figure 1.2

Composite three-dimensional difference Fourier synthesis viewed down the b-axis showing the hydrogen atoms. The contours are drawn at intervals of 0.1 $e\text{Å}^{-3}$. The first contour is at 0.2 $e\text{Å}^{-3}$ except around H(2), H(5), and H(5), where it is at 0.3 $e\text{Å}^{-3}$.


0
a
c/2
O
O
O
O
O
O
S
O1
O2
1
2
3
4
5
7
8
10
11
12
13
14
151
152
153

hydrogen atoms isotropically were carried out. Atomic scattering factors for bonded hydrogen (Stewart, Davidson, and Simpson, 1965) were used. A shift factor of 0.8 was applied throughout the block-diagonal refinement. In the last cycle no shifts were larger than 0.5σ for the hydrogen atoms and 0.1σ for the other atoms and the final value of R was 9.8%.

Lingafelter and Donohue (1966) showed that if data are collected along only one axis, this leads to degeneracy between the individual layer-scale factors and the anisotropic temperature parameters in full-matrix least-squares refinement. However, this was avoided since the block-diagonal approximation was used for the anisotropic refinement.

At the end of the refinement the agreement analysis of averaged $w\Delta^2$ as a function of $|F_o|$ and of $\sin\theta/\lambda$ was:

$\|F_o\|$	$\langle w\Delta^2 \rangle$	No. of reflexions	$\sin\theta/\lambda$	$\langle w\Delta^2 \rangle$	No. of reflexions
0- 9	0.098	1162	0.0-0.2	0.132	87
9- 18	0.131	519	0.2-0.4	0.137	581
18- 36	0.150	285	0.4-0.6	0.110	1150
36- 72	0.162	76	0.6-0.8	0.091	245
72-144	0.149	21			

As can be seen there is little variation in $\langle w\Delta^2 \rangle$ in both

cases. The type of weighting scheme and its parameters are thus appropriate for these data.

The progress of the least-squares refinement was

($R = \sum_{hk\ell} |\Delta| / \sum_{hk\ell} |F_o|$; $R' = \sum_{hk\ell} w\Delta^2 / \sum_{hk\ell} w F_o^2$) :

Cycle No.	R	R'	Parameters refined	Type of refinement
1	0.252	0.123	x,y,z, U_{iso} for S, O, C + layer-scale factors	full matrix
2	0.217	0.0797		
3	0.213	0.0762		
4	0.213	0.0759		
5	0.130	0.0320	x,y,z, U_{ij} (i,j = 1,2,3) for S, O, C + layer-scale factors	block diagonal
6	0.119	0.0276		
7	0.118	0.0263		
8*	0.117	0.0268	as above (S, O corrected for $\Delta f', \Delta f''$)	
9	0.104	0.0225	as above + x,y,z, U_{iso} for H	
10	0.102	0.0209		
11	0.099	0.0195		
12	0.098	0.0191		
13	0.098	0.0190		
14	0.098	0.0189		
15	0.098	0.0188	-	(structure factors only).

*Adjustments in the parameters of the weighting scheme were made.

Tables 1.1, 1.2, and 1.3 list, respectively, the coordinates for non-hydrogen atoms, their anisotropic thermal parameters, and coordinates and isotropic thermal parameters for hydrogen atoms, together with e.s.d.'s derived from the inverse of the least-squares matrix. The final observed and calculated structure factors are given in Table 1.4. Orthogonal coordinates in Ångstrøm, referred to the axes a^*, b, and c, for non-hydrogen atoms and for hydrogen atoms are listed in Tables 1.5 and 1.6.

TABLE 1.1

FRACTIONAL COORDINATES AND E.S.D.s

ATOM	x/a	y/b	z/c
S(1)	0.5004 ± 1	0.2918 ± 1	0.4035 ± 1
O(1)	0.6289 ± 4	0.3501 ± 4	0.4224 ± 4
O(2)	0.5187 ± 5	0.2390 ± 4	0.5030 ± 3
O(3)	0.3673 ± 4	0.3933 ± 3	0.3512 ± 3
C(1)	0.3089 ± 4	0.4524 ± 5	0.2411 ± 4
C(2)	0.2546 ± 5	0.5715 ± 5	0.2276 ± 4
C(3)	0.1858 ± 5	0.6339 ± 5	0.1199 ± 5
C(4)	0.1776 ± 5	0.5768 ± 5	0.0308 ± 4
C(5)	0.2348 ± 5	0.4578 ± 5	0.0467 ± 4
C(6)	0.3036 ± 4	0.3897 ± 4	0.1530 ± 4
C(7)	0.3722 ± 5	0.2613 ± 5	0.1698 ± 4
C(8)	0.4069 ± 4	0.1879 ± 5	0.2775 ± 4
C(9)	0.2743 ± 4	0.1198 ± 4	0.2579 ± 3
C(10)	0.1284 ± 5	0.1726 ± 5	0.1954 ± 5
C(11)	0.0073 ± 5	0.1050 ± 6	0.1737 ± 5
C(12)	0.0291 ± 5	-0.0153 ± 5	0.2126 ± 4
C(13)	0.1754 ± 6	-0.0692 ± 5	0.2767 ± 5
C(14)	0.2959 ± 5	-0.0018 ± 5	0.2981 ± 4
C(15)	0.2780 ± 7	0.1813 ± 5	0.0568 ± 5

TABLE 1.2

ANISOTROPIC TEMPERATURE PARAMETERS AND E.S.D.s (A^{o2})

ATOM	U 11	U 22	U 33	2U 23	2U 31	2U 12
S(1)	0.0291 5	0.0497 8	0.0372 5	-0.0001 9	0.0085 8	0.0082 9
O(1)	0.0316 15	0.0531 25	0.0799 26	-0.0193 41	0.0312 34	-0.0160 32
O(2)	0.0608 23	0.0812 31	0.0372 17	0.0125 37	0.0219 33	0.0232 44
O(3)	0.0430 15	0.0546 23	0.0380 15	0.0054 28	0.0399 27	0.0216 29
C(1)	0.0265 16	0.0485 31	0.0351 19	0.0032 36	0.0260 30	-0.0001 34
C(2)	0.0390 21	0.0474 32	0.0468 23	-0.0021 42	0.0433 39	0.0118 40
C(3)	0.0386 22	0.0473 34	0.0638 29	0.0103 49	0.0494 44	0.0069 43
C(4)	0.0444 22	0.0538 34	0.0495 25	0.0207 46	0.0449 41	0.0014 45
C(5)	0.0417 20	0.0515 32	0.0410 21	0.0005 42	0.0450 37	-0.0082 42
C(6)	0.0267 16	0.0473 30	0.0390 19	-0.0034 37	0.0339 31	-0.0065 34
C(7)	0.0328 20	0.0495 31	0.0504 24	-0.0038 42	0.0502 39	0.0028 37
C(8)	0.0230 16	0.0403 29	0.0396 20	-0.0113 36	0.0203 31	0.0025 32
C(9)	0.0251 16	0.0387 28	0.0343 18	0.0058 34	0.0202 30	0.0041 32

C(10)	0.0287 19	0.0418 33	0.0691 30	0.0390 48	0.0381 41	0.0169 38
C(11)	0.0279 19	0.0701 42	0.0673 31	0.0280 56	0.0349 41	0.0022 44
C(12)	0.0447 24	0.0610 37	0.0508 26	-0.0143 47	0.0512 43	-0.0355 46
C(13)	0.0655 30	0.0435 35	0.0658 30	0.0094 51	0.0843 53	0.0008 50
C(14)	0.0431 22	0.0427 33	0.0528 25	0.0121 43	0.0516 41	0.0157 40
C(15)	0.0781 36	0.0534 37	0.0579 29	-0.0176 53	0.0869 58	0.0018 58

TABLE 1.3

HYDROGEN-ATOM FRACTIONAL COORDINATES, ISOTROPIC TEMPERATURE PARAMETERS AND E.S.D.s

ATOM	x/a	y/b	z/c	U (A^{o2})
H(2)	0.254 ± 6	0.597 ± 5	0.286 ± 5	0.0596 ± 147
H(3)	0.151 ± 7	0.724 ± 5	0.113 ± 5	0.0737 ± 169
H(4)	0.127 ± 9	0.607 ± 7	-0.050 ± 7	0.1063 ± 230
H(5)	0.239 ± 6	0.432 ± 5	-0.009 ± 4	0.0514 ± 135
H(7)	0.460 ± 7	0.275 ± 5	0.176 ± 6	0.0743 ± 174
H(8)	0.490 ± 5	0.126 ± 5	0.299 ± 4	0.0499 ± 132
H(10)	0.115 ± 6	0.255 ± 5	0.182 ± 4	0.0453 ± 126
H(11)	-0.093 ± 6	0.152 ± 5	0.125 ± 5	0.0627 ± 155
H(12)	-0.069 ± 8	-0.056 ± 6	0.190 ± 7	0.1012 ± 208
H(13)	0.206 ± 9	-0.137 ± 8	0.317 ± 7	0.1212 ± 250
H(14)	0.408 ± 7	-0.027 ± 6	0.350 ± 6	0.0790 ± 187
H(15)	0.332 ± 6	0.106 ± 5	0.079 ± 5	0.0602 ± 152
$H(15)^1$	0.163 ± 7	0.179 ± 6	0.018 ± 5	0.0850 ± 184
$H(15)^2_3$	0.286 ± 6	0.201 ± 5	-0.002 ± 5	0.0637 ± 161

TABLE 1.4

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|Fo|	|Fc|
0	0	2	66.6	70.7
0	0	4	28.0	23.3
0	0	6	16.5	16.4
0	0	8	6.9	7.4
0	0	10	7.3	7.4
0	0	12	9.2	9.1
1	0	0	98.0	103.6
1	0	2	96.3	105.0
1	0	4	17.1	16.2
1	0	6	9.1	8.7
1	0	8	22.5	23.6
1	0	10	10.0	10.3
1	0	12	12.8	13.9
2	0	0	41.2	38.2
2	0	2	27.0	24.3
2	0	4	13.3	12.6
2	0	6	2.2	2.4
2	0	10	19.5	20.5
2	0	12	6.0	7.1
3	0	0	3.5	3.9
3	0	2	56.2	53.1
3	0	4	12.9	13.2
3	0	6	14.3	15.2
3	0	10	14.5	15.9
4	0	0	45.5	43.9
4	0	2	13.7	13.8
4	0	4	19.4	19.7
4	0	6	21.8	24.5
4	0	8	11.2	11.8
4	0	10	8.0	11.3
5	0	0	23.5	22.2
5	0	2	3.2	3.4
5	0	4	7.2	7.1
5	0	6	13.4	15.9
5	0	8	7.7	8.9
6	0	0	48.0	45.1
6	0	2	9.7	9.9
6	0	4	25.9	28.3
6	0	6	8.8	8.3
7	0	0	13.0	12.9
7	0	2	29.4	32.7
7	0	4	23.2	25.8
7	0	6	10.1	11.2
8	0	0	32.2	32.9
8	0	2	3.7	3.9
8	0	4	9.6	11.1
9	0	0	26.4	28.6
9	0	2	5.7	5.6
10	0	0	18.6	21.2
11	0	0	4.4	5.3
1	0	-2	28.0	24.4
1	0	-4	77.1	73.1
1	0	-6	35.4	37.7
1	0	-8	6.8	6.6
1	0	-10	15.7	16.2
1	0	-12	15.9	17.6
2	0	-2	57.0	56.6
2	0	-4	93.7	95.8
2	0	-6	20.2	19.2
2	0	-8	9.7	8.8
2	0	-10	58.6	59.0
2	0	-12	14.0	14.6
3	0	-2	2.1	2.5
3	0	-4	103.6	109.5
3	0	-6	34.3	33.3
3	0	-8	21.3	22.8
3	0	-10	42.2	39.8
3	0	-12	51.9	54.3
4	0	-2	16.3	15.9
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23	8	6	2.3	2.3
23	8	7	2.3	2.3
23	8	8	2.3	2.3
23	8	9	2.3	2.3
24	8	0	2.3	2.3
24	8	1	2.3	2.3
24	8	2	2.3	2.3
24	8	3	2.3	2.3
24	8	4	2.3	2.3
24	8	5	2.3	2.3
24	8	6	2.3	2.3
24	8	7	2.3	2.3
24	8	8	2.3	2.3
24	8	9	2.3	2.3
25	8	0	2.3	2.3
25	8	1	2.3	2.3
25	8	2	2.3	2.3
25	8	3	2.3	2.3
25	8	4	2.3	2.3
25	8	5	2.3	2.3
25	8	6	2.3	2.3
25	8	7	2.3	2.3
25	8	8	2.3	2.3
25	8	9	2.3	2.3
26	8	0	2.3	2.3
26	8	1	2.3	2.3
26	8	2	2.3	2.3
26	8	3	2.3	2.3
26	8	4	2.3	2.3
26	8	5	2.3	2.3
26	8	6	2.3	2.3
26	8	7	2.3	2.3
26	8	8	2.3	2.3
26	8	9	2.3	2.3
27	8	0	2.3	2.3
27	8	1	2.3	2.3
27	8	2	2.3	2.3
27	8	3	2.3	2.3
27	8	4	2.3	2.3
27	8	5	2.3	2.3
27	8	6	2.3	2.3
27	8	7	2.3	2.3
27	8	8	2.3	2.3
27	8	9	2.3	2.3
28	8	0	2.3	2.3
28	8	1	2.3	2.3
28	8	2	2.3	2.3
28	8	3	2.3	2.3
28	8	4	2.3	2.3
28	8	5	2.3	2.3
28	8	6	2.3	2.3
28	8	7	2.3	2.3
28	8	8	2.3	2.3
28	8	9	2.3	2.3
29	8	0

TABLE 1.5

ORTHOGONAL COORDINATES IN ANGSTRØM AND E.S.D.s

ATOM	X'	Y	Z'
S(1)	4.3106 ± 9	3.1218 ± 13	2.2523 ± 12
O(1)	5.4177 ± 31	3.7461 ± 41	1.6086 ± 45
O(2)	4.4681 ± 40	2.5570 ± 46	3.5575 ± 41
O(3)	3.1639 ± 31	4.2083 ± 35	2.4472 ± 31
C(1)	2.6611 ± 37	4.8409 ± 49	1.2757 ± 40
C(2)	2.1935 ± 42	6.1155 ± 51	1.4667 ± 47
C(3)	1.6004 ± 45	6.7829 ± 56	0.4052 ± 55
C(4)	1.5296 ± 47	6.1721 ± 57	-0.8220 ± 50
C(5)	2.0228 ± 44	4.8988 ± 52	-1.0006 ± 44
C(6)	2.6151 ± 36	4.1701 ± 47	0.0429 ± 40
C(7)	3.2062 ± 40	2.7957 ± 51	-0.2046 ± 44
C(8)	3.5048 ± 36	2.0102 ± 48	1.1024 ± 44
C(9)	2.3627 ± 35	1.2813 ± 46	1.7641 ± 40
C(10)	1.1063 ± 41	1.8464 ± 54	1.9024 ± 59
C(11)	0.0629 ± 44	1.1237 ± 61	2.4533 ± 62
C(12)	0.2503 ± 47	-0.1637 ± 59	2.8585 ± 48
C(13)	1.5110 ± 56	-0.7408 ± 57	2.7400 ± 53
C(14)	2.5493 ± 46	-0.0194 ± 50	2.1899 ± 49
C(15)	2.3946 ± 63	1.9402 ± 58	-1.1621 ± 54

TABLE 1.6

ORTHOGONAL COORDINATES IN Å ANGSTRØM AND E.S.D.s OF HYDROGEN ATOMS

ATOM	X'	Y	Z'
H(2)	2.19 ± 5	6.39 ± 5	2.31 ± 5
H(3)	1.30 ± 6	7.75 ± 6	0.56 ± 6
H(4)	1.09 ± 7	6.50 ± 7	-1.62 ± 7
H(5)	2.06 ± 5	4.62 ± 5	-1.84 ± 4
H(7)	3.97 ± 6	2.95 ± 6	-0.74 ± 6
H(8)	4.22 ± 5	1.35 ± 5	0.82 ± 4
H(10)	0.99 ± 5	2.73 ± 5	1.81 ± 5
H(11)	-0.80 ± 5	1.63 ± 6	2.46 ± 5
H(12)	-0.59 ± 7	-0.60 ± 7	3.23 ± 7
H(13)	1.78 ± 8	-1.47 ± 8	3.11 ± 7
H(14)	3.51 ± 6	-0.29 ± 6	2.14 ± 6
H(15)	2.86 ± 5	1.13 ± 5	-1.23 ± 5
$H(15)_1$	1.41 ± 6	1.91 ± 6	-0.91 ± 6
$H(15)_2$	2.46 ± 5	2.16 ± 5	-2.07 ± 5
$H(15)_3$			

6. Rigid-body thermal vibration

The thermal vibrations were analysed in terms of rigid-body vibration (Cruickshank, 1956b) and libration corrections were applied to the positional parameters (Cruickshank, 1961a). Molecular dimensions deduced from these coordinates are labelled "corrected". The hydrogen atoms were excluded from these calculations.

The vibration tensor $\underline{T}$ and libration tensor $\underline{\omega}$ were determined by minimising $M = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{r=1}^{N} w_{ij}^{r} (U_{ij,obs}^{r} - U_{ij,calc}^{r})^2$ by the least-squares method. The weights, $w_{ij}^{r} = 1/\sigma^2 (U_{ij,obs}^{r})$, were applied to each term. The main results of this analysis are given in Table 1.7. The molecular vibration is approximately that of a rigid body even though some of the calculated U_{ij}'s differ significantly from the observed ones. This indicates that a better approximation could possibly have been achieved if a "screw" (or "helical") motion had been taken into account in addition to the vibration and libration motions. Schomaker and Trueblood (1968) suggested this treatment for non-centrosymmetric molecules. The differences between $U_{ij,obs}$ and $U_{ij,calc}$ are larger for some of the atoms in the aromatic ring C than for most of the other atoms. This indicates that additional motion occurs in this ring. The

coordinates of some of these atoms may therefore contain a systematic error since they have not been corrected for this additional oscillation.

Both vibration and libration are anisotropic, the latter more markedly so. The axis of maximum libration is approximately parallel to the inertial X-axis (the axis of minimum inertia). Figure 1.3 shows the sultone B molecule relative to the inertial X and Y axes viewed down the inertial Z-axis.

The maximum libration of the molecule is approximately 5° and the effect of the librational correction was therefore small. Most of the bond lengths increased by about 0.003 Å - the largest increase was in the S-C(8) bond (0.006 Å). The maximum change in any of the angles was 0.2°. Corrected and uncorrected bond lengths and angles with their e.s.d.'s are given in Tables 1.8 and 1.9, respectively. Non-bonded distances (corrected) are shown in Table 1.10.

TABLE 1.7

MOLECULAR VIBRATION ANALYSIS.

(a)Principal values of vibration tensors and their direction cosines referred to orthogonal axes.

ATOM	$U(A^{o2})$	D1	D2	D3
S(1)	0.0809	-0.3440	-0.1480	0.9272
	0.0221	0.9381	-0.0977	0.3324
	0.0493	0.0414	0.9841	0.1724
O(1)	0.1235	-0.0571	-0.0770	0.9954
	0.0284	0.9428	0.3237	0.0792
	0.0555	-0.3284	0.9430	0.0541
O(2)	0.0319	0.7952	-0.1696	0.5822
	0.1106	-0.6054	-0.2767	0.7463
	0.0803	0.0346	-0.9459	-0.3227
O(3)	0.0671	-0.5154	-0.6763	0.5263
	0.0342	0.8533	-0.3482	0.3882
	0.0470	-0.0793	0.6491	0.7565
C(1)	0.0254	0.9780	-0.0170	0.2080
	0.0517	-0.1661	0.5405	0.8248
	0.0472	-0.1264	-0.8412	0.5258
C(2)	0.0634	-0.2527	-0.4320	0.8657
	0.0359	0.8980	-0.4379	0.0436
	0.0461	0.3602	0.7884	0.4986
C(3)	0.0813	0.0120	0.1132	0.9935
	0.0374	0.9410	-0.3373	0.0270
	0.0481	0.3381	0.9346	-0.1106
C(4)	0.0750	-0.1972	0.5031	0.8414
	0.0396	0.7763	-0.4440	0.4474
	0.0491	0.5987	0.7414	-0.3031
C(5)	0.0570	-0.3935	0.6950	0.6017
	0.0386	0.9046	0.1761	0.3882
	0.0468	0.1639	0.6971	-0.6980

C(6)	0.0262	0.0000	0.0000	0.0000
	0.0482	-0.1199	0.7757	0.6196
	0.0472	0.0938	-0.6125	0.7849
C(7)	0.0312	-0.9591	0.1236	0.2545
	0.0563	0.1786	-0.4329	0.8835
	0.0482	0.2194	0.8929	0.3932
C(8)	0.0645	-0.1416	-0.3301	0.9333
	0.0221	0.9886	0.0013	0.1505
	0.0373	-0.0508	0.9440	0.3261
C(9)	0.0553	-0.2386	0.0907	0.9669
	0.0228	0.9556	-0.1554	0.2504
	0.0390	0.1730	0.9837	-0.0496
C(10)	0.1010	0.0482	0.3016	0.9522
	0.0237	0.8472	-0.5174	0.1210
	0.0410	0.5292	0.8008	-0.2805
C(11)	0.1038	0.0015	0.4557	0.8901
	0.0279	0.9994	-0.0320	0.0147
	0.0613	0.0352	0.8896	-0.4555
C(12)	0.0333	0.8426	0.5385	0.0091
	0.0754	-0.4920	0.7629	0.4194
	0.0582	0.2189	-0.3579	0.9077
C(13)	0.0421	0.0112	-0.9702	0.2421
	0.0669	0.4049	0.2258	0.8861
	0.0652	-0.9143	0.0881	0.3953
C(14)	0.0348	0.6977	-0.7109	0.0879
	0.0633	-0.0957	0.0291	0.9950
	0.0507	-0.7099	-0.7027	-0.0477
C(15)	0.0426	0.1351	0.7347	0.6648
	0.0820	-0.8939	-0.1990	0.4017
	0.0646	0.4274	-0.6485	0.6299

(b) Centre of mass, referred to orthogonal axes.

X'	Y	Z'
2.6983	3.0181	1.4385

(c) Principal moments of inertia, I, and direction cosines D1,D2,D3, of inertial axes referred to orthogonal axes.

I ($gcm^2 \times 10^{-40}$)	D1	D2	D3
1345	-0.1347	-0.9120	0.3874
2965	-0.4443	0.4051	0.7991
2449	-0.8857	-0.0645	-0.4597

(d) $\underline{T}$ and $\underline{\omega}$ and their e.s.d.s, referred to inertial axes.

$$\underline{T}(A^{o2}) = \begin{bmatrix} 0.0505 & 0.0085 & -0.0003 \\ 15 & 28 & 23 \\ & 0.0466 & -0.0078 \\ & 35 & 27 \\ & & 0.0237 \\ & & 16 \end{bmatrix}$$

$$\underline{\omega}(^{o2}) = \begin{bmatrix} 23.4 & -2.3 & -1.2 \\ 3.1 & 1.6 & 1.6 \\ & 6.0 & 0.4 \\ & 1.0 & 1.4 \\ & & 2.3 \\ & & 1.5 \end{bmatrix}$$

(e) The principal values for $\underline{T}$ and $\underline{\omega}$ and their direction components referred to crystal axes.

$\underline{T}(\text{Å}^2)$	D1	D2	D3
0.0211	-1.286	0.140	-1.047
0.0580	0.330	0.402	-0.670
0.0416	0.050	-0.905	-0.456

$\underline{\omega}(^{o2})$	D1	D2	D3
23.8	-0.030	0.951	-0.288
2.3	1.106	0.142	1.209
5.7	-0.679	0.273	0.375

(f) U obs - U calc, with respect to inertial axes.

ATOM	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
S(1)	0.0019	0.0004	0.0000	0.0001	0.0016	0.0079
O(1)	0.0039	0.0017	0.0142	-0.0062	-0.0327	0.0209
O(2)	0.0256	0.0070	0.0067	0.0006	0.0216	0.0018
O(3)	0.0081	-0.0048	0.0058	0.0004	0.0185	-0.0051
C(1)	-0.0035	0.0010	-0.0029	0.0016	-0.0005	-0.0203
C(2)	0.0032	-0.0019	-0.0075	0.0066	-0.0010	-0.0027
C(3)	-0.0035	0.0048	-0.0040	-0.0059	-0.0190	-0.0054
C(4)	-0.0096	-0.0028	-0.0037	-0.0059	-0.0148	-0.0240
C(5)	-0.0081	-0.0106	-0.0057	-0.0069	-0.0199	-0.0241
C(6)	-0.0058	-0.0056	-0.0015	-0.0046	-0.0141	-0.0213
C(7)	-0.0006	-0.0053	-0.0026	-0.0122	-0.0120	-0.0138
C(8)	-0.0017	-0.0002	-0.0053	0.0024	-0.0132	0.0064
C(9)	-0.0102	0.0018	-0.0039	-0.0006	0.0030	-0.0073
C(10)	-0.0149	0.0204	0.0142	-0.0345	0.0135	-0.0020
C(11)	0.0031	0.0059	-0.0065	0.0007	0.0168	-0.0261
C(12)	-0.0031	-0.0123	-0.0174	0.0538	-0.0016	-0.0349
C(13)	-0.0082	0.0008	0.0117	0.0222	0.0134	-0.0087
C(14)	-0.0037	0.0021	0.0057	-0.0016	0.0086	-0.0017
C(15)	0.0044	-0.0047	0.0024	-0.0068	-0.0078	0.0016

Figure 1.3

A view of the sultone B molecule relative to the inertial X and Y axes.

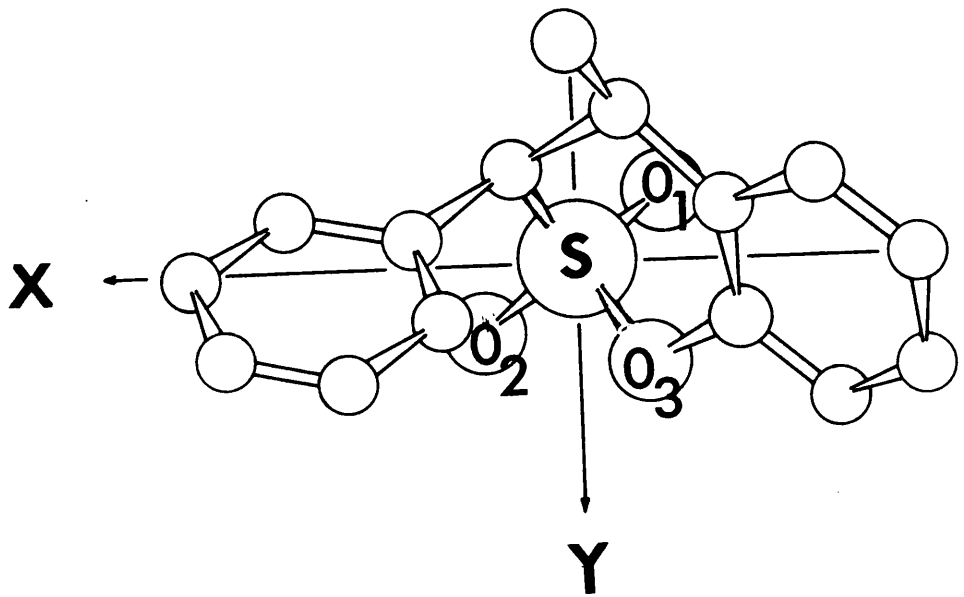

X
S
O1
O2
O3
Y

TABLE 1.8

BOND LENGTHS

Bond	Uncorrected length	Corrected length	E.s.d.
S(1)-O(1)	1.425 Å	1.428 Å	0.004 Å
S(1)-O(2)	1.431	1.434	0.004
S(1)-O(3)	1.592	1.595	0.004
S(1)-C(8)	1.791	1.797	0.005
O(3)-C(1)	1.423	1.426	0.005
C(6)-C(7)	1.517	1.519	0.007
C(8)-C(9)	1.508	1.512	0.006
C(7)-C(8)	1.554	1.557	0.006
C(7)-C(15)	1.519	1.523	0.007
C(1)-C(2)	1.371	1.373	0.007
C(2)-C(3)	1.387	1.390	0.007
C(3)-C(4)	1.373	1.377	0.008
C(4)-C(5)	1.377	1.379	0.008
C(5)-C(6)	1.404	1.406	0.006
C(6)-C(1)	1.404	1.409	0.006
C(9)-C(10)	1.385	1.389	0.006
C(10)-C(11)	1.384	1.386	0.007
C(11)-C(12)	1.363	1.363	0.008
C(12)-C(13)	1.392	1.395	0.007
C(13)-C(14)	1.379	1.382	0.007
C(14)-C(9)	1.381	1.382	0.007

Bond	Uncorrected length	E.s.d.
C(2)-H(2)	0.89 Å	0.05 Å
C(3)-H(3)	1.02	0.06
C(4)-H(4)	0.97	0.07
C(5)-H(5)	0.88	0.05
C(10)-H(10)	0.90	0.05
C(11)-H(11)	1.00	0.05
C(12)-H(12)	1.02	0.07
C(13)-H(13)	0.86	0.08
C(14)-H(14)	1.00	0.06
C(7)-H(7)	0.94	0.06
C(8)-H(8)	1.01	0.05
$C(15)-H(15)_3$	0.93	0.05
$C(15)-H(15)_2$	1.02	0.06
$C(15)-H(15)_1$	0.94	0.06

TABLE 1.9

BOND ANGLES

Angle	Uncorrected angle	Corrected angle	E.s.d.
O(1)-S(1)-O(2)	120.0°	119.9°	0.2°
O(1)-S(1)-O(3)	108.4	108.6	0.2
O(2)-S(1)-O(3)	103.7	103.6	0.2
O(1)-S(1)-C(8)	109.4	109.3	0.2
O(2)-S(1)-C(8)	113.0	113.1	0.2
O(3)-S(1)-C(8)	100.3	100.2	0.2
S(1)-O(3)-C(1)	117.2	117.1	0.3
O(3)-C(1)-C(2)	114.8	114.7	0.4
O(3)-C(1)-C(6)	121.5	121.6	0.4
C(2)-C(1)-C(6)	123.7	123.7	0.4
C(1)-C(2)-C(3)	119.1	119.0	0.4
C(2)-C(3)-C(4)	119.5	119.6	0.5
C(3)-C(4)-C(5)	120.6	120.6	0.5
C(4)-C(5)-C(6)	122.3	122.2	0.4
C(1)-C(6)-C(5)	114.7	114.8	0.4
C(1)-C(6)-C(7)	124.3	124.3	0.4
C(5)-C(6)-C(7)	120.9	120.8	0.4
C(6)-C(7)-C(8)	113.3	113.2	0.4
C(6)-C(7)-C(15)	113.9	113.8	0.4
C(8)-C(7)-C(15)	110.4	110.5	0.4
S(1)-C(8)-C(7)	108.2	108.4	0.3
S(1)-C(8)-C(9)	111.1	111.0	0.3
C(7)-C(8)-C(9)	117.9	117.8	0.3
C(8)-C(9)-C(10)	122.3	122.4	0.4
C(8)-C(9)-C(14)	119.2	119.1	0.4
C(10)-C(9)-C(14)	118.4	118.4	0.4
C(9)-C(10)-C(11)	120.7	120.8	0.5
C(10)-C(11)-C(12)	120.5	120.5	0.5
C(11)-C(12)-C(13)	119.4	119.4	0.5
C(12)-C(13)-C(14)	120.0	120.1	0.5
C(9)-C(14)-C(13)	120.9	120.8	0.4

Angle	Uncorrected angle	E.s.d.
H(2)-C(2)-C(1)	115°	3°
H(2)-C(2)-C(3)	125	3
H(3)-C(3)-C(4)	123	3
H(3)-C(3)-C(2)	118	3
H(4)-C(4)-C(5)	112	4
H(4)-C(4)-C(3)	128	4
H(5)-C(5)-C(4)	115	3
H(5)-C(5)-C(6)	122	3
H(10)-C(10)-C(9)	121	3
H(10)-C(10)-C(11)	117	3
H(11)-C(11)-C(12)	127	3
H(11)-C(11)-C(10)	113	3
H(12)-C(12)-C(11)	113	4
H(12)-C(12)-C(13)	127	4
H(13)-C(13)-C(14)	112	5
H(13)-C(13)-C(12)	127	5
H(14)-C(14)-C(9)	112	4
H(14)-C(14)-C(13)	127	4
H(7)-C(7)-C(15)	99	4
H(7)-C(7)-C(6)	105	4
H(7)-C(7)-C(8)	114	4
H(8)-C(8)-C(9)	110	3
H(8)-C(8)-C(7)	103	3
H(8)-C(8)-S(1)	106	3
$H(15)_3$-C(15)-$H(15)_2$	109	5
$H(15)_3$-C(15)-$H(15)_1$	95	5
$H(15)_2$-C(15)-$H(15)_1$	119	5
$H(15)_3$-C(15)-C(7)	116	3
$H(15)_2$-C(15)-C(7)	112	3
$H(15)_1$-C(15)-C(7)	105	3

TABLE 1.10

NON-BONDED DISTANCES (CORRECTED)

(a) Some intramolecular distances

Heterocyclic ring		Methyl group	
O(2)...O(3)	2.383 Å	C(15)...C(9)	3.006 Å
O(1)...O(3)	2.456	C(15)...C(5)	2.989
O(1)...O(2)	2.477	C(15)...H(5)	2.79
O(1)...C(8)	2.639	$H(15)_3$...H(5)	2.51
O(2)...C(8)	2.702		
O(1)...C(1)	2.993	Phenyl group	
O(1)...C(7)	3.024		
O(2)...C(9)	3.056	C(10)...C(1)	3.437
O(3)...C(10)	3.188	C(10)...C(6)	3.342
S(1)...C(10)	3.479	H(10)...C(1)	2.74
S(1)...C(14)	3.609	H(10)...C(6)	2.80
		H(14)...H(8)	2.23

(b) Intermolecular distances (<3.5 Å) of non-hydrogen atoms

$O(1)...C(3)_{I}$	3.407 Å
$O(1)...C(4)_{I}$	3.436
$O(2)...C(13)_{II}$	3.348
$O(2)...C(14)_{II}$	3.368
$O(2)...C(15)_{III}$	3.347
$O(1)...C(11)_{IV}$	3.406

The subscripts refer to the following equivalent positions:

I $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$

II $(1-x, -y, 1-z)$

III $(x, \frac{1}{2}-y, \frac{1}{2}+z)$

IV $(1+x), \frac{1}{2}-y, 1+z)$

7. Description and discussion of the structure

This crystal structure determination (Bjåmer and Ferguson, 1967) shows that in sultone B the methyl and the phenyl groups are *cis* to each other. The heterocyclic ring is found to be in a distorted half-chair conformation with the phenyl ring axial and the methyl group quasi-equatorial (Barton and Cookson, 1956). The oxygen O(1) is axial and O(2) is equatorial. A view of the molecule in the [001] direction and the numbering scheme are given in Figure 1.4.

The atoms of aromatic ring A (C(1)....C(6)) are coplanar and their r.m.s. distance from the plane is 0.006 Å. (The least-squares planes and displacements of atoms from them are listed in Table 1.11). The hydrogen atoms H(2), H(3), H(4), and H(5) were not included in the calculation of the plane of ring A. However, none of their displacements are significant.

There is a great deal of strain present in ring B which may be caused by the considerable variation in bond lengths within this ring. The atoms O(3) and C(7) which theoretically should have been in the plane of the aromatic

Figure 1.4

A view of the sultone B molecule, projected on (001), with the numbering scheme.

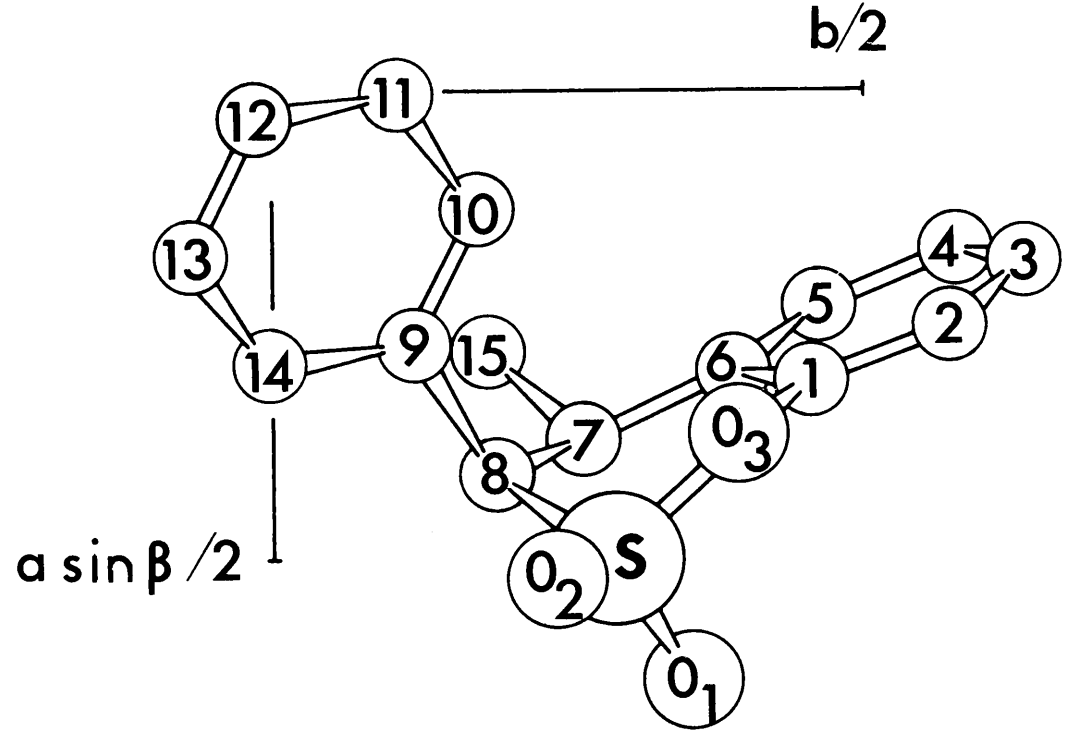

b/2
a sin β /2
11
12
10
13
9
14
15
4
3
5
2
6
1
7
O_3
8
S
O_2
O_1

TABLE 1.11

LEAST-SQUARES PLANES

Plane 1 Aromatic ring A		Plane 2 Ring B		Plane 3 Aromatic ring C	
Atom	Δ	Atom	Δ	Atom	Δ
C(1)	-0.007 Å	C(1)	0.027 Å	C(9)	-0.003 Å
C(2)	0.010	C(6)	-0.026	C(10)	0.000
C(3)	-0.007	C(7)	0.012	C(11)	0.005
C(4)	0.000	O(3)	-0.013	C(12)	-0.007
C(5)	0.003			C(13)	0.005
C(6)	0.001			C(14)	0.000
r.m.s.d. =	0.006	r.m.s.d. =	0.021	r.m.s.d. =	0.004
χ^2 =	5.72	χ^2 =	61.84	χ^2 =	3.57
O(3)*	-0.085	C(8)*	-0.299	C(8)*	-0.081
C(7)*	0.070	S(1)*	0.628	H(8)*	-0.383
H(2)*	-0.097	C(9)*	-1.750	H(10)*	0.182
H(3)*	0.055	C(15)*	-0.859	H(11)*	-0.032
H(4)*	-0.066	O(1)*	2.001	H(12)*	-0.022
H(5)*	0.141	O(2)*	0.277	H(13)*	0.166
				H(14)*	0.107

*These atoms were not used to calculate the least-squares plane.

Plane	Equations for the least-squares planes
1	$0.892\ X' + 0.379\ Y - 0.246\ Z' = 3.903$ Å
2	$0.895\ X' + 0.395\ Y - 0.206\ Z' = 4.007$
3	$0.247\ X' + 0.332\ Y + 0.911\ Z' = 2.615$

(X', Y, and Z' are orthogonal coordinates (in Å) referred to the axes a*, b, and c, i.e. $X' = X\sin\beta$ and $Z' = Z + X\cos\beta$).

ring A are significantly displaced from it, each in opposite direction. Hence the atoms C(1), C(6), C(7), and O(3) of ring B are not coplanar (χ^2 for the four atoms of the least-squares plane has the high value of 61.8); the "best" plane makes a dihedral angle of 7.9° with the aromatic plane. The distortion of the half-chair in ring B is further expressed by the unequal displacements of C(8) and S(1) from the "best" plane, viz. -0.299 and +0.628 Å, respectively. For comparison it can be mentioned that in a regular half-chair conformation of cyclohexene, four atoms are in one plane and the other two displaced by ±0.43 Å (Corey and Sneen, 1955).

The atoms (C(9)....C(14)) of phenyl ring C are coplanar and their r.m.s. distance from the plane is 0.004 Å. The dihedral angle between the two aromatic planes is 83°, and the orientation of the ring-C plane is such that it intersects the C(1)-C(6) bond approximately at its midpoint. The hydrogen atoms are coplanar with the phenyl ring except H(10) which deviates by 0.182 Å (i.e. 3.6σ) from it. As will be seen from the following discussion no significance should be ascribed to this deviation. Carbon atom C(8) is displaced from this plane by 0.081 Å, a highly significant deviation (19σ). This deviation may be caused by repulsive forces between the methyl and the phenyl groups.

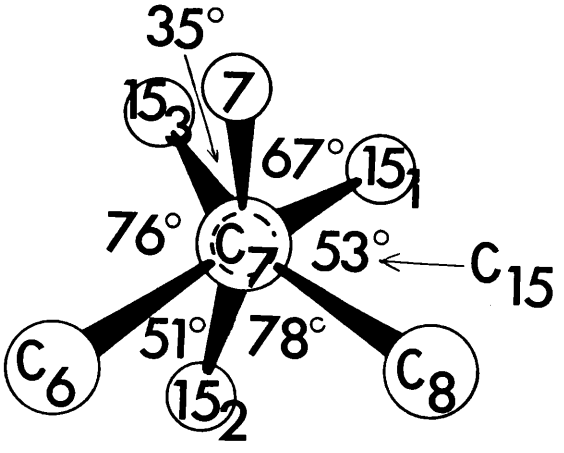
The strain is diminished by bending the phenyl ring away from the methyl group.

The hydrogen atoms of the methyl group are not completely staggered with respect to the substituents at C(7). This can be seen by looking down the C(7)-C(15) bond (Figure 1.5) and it is probably due to repulsion between H(5) and $H(15)_3$.

The aromatic C-C bond lengths vary from 1.363 ± 0.008 Å to 1.409 ± 0.006 Å with an average of 1.386 ± 0.003 Å. The shortest of them, C(11)-C(12), is 3.9σ shorter than the normal value 1.394 ± 0.005 Å (Sutton, 1965). Of the two C_{sp^3}-C_{sp^3} bonds, C(7)-C(8) and C(7)-C(15), the former (1.557 ± 0.006 Å) is 3.3σ longer than the accepted value 1.537 ± 0.005 Å (Sutton, 1965). The e.s.d.'s were derived from least-squares refinement in which the block-diagonal approximation was used and in the calculations of bond lengths correlations between atoms were not taken into account. It is therefore probable that the e.s.d.'s are underestimated and it seems reasonable to increase their values by 50%. In view of this the deviations in the two bond lengths mentioned above should not be considered significant at a 0.1% significance level. Both C_{sp^2}-C_{sp^3} bonds, C(8)-C(9) and C(6)-C(7), agree with the value 1.505 ± 0.005 Å given by Sutton (1965).

Figure 1.5

View down the C(7)-C(15) bond showing the orientation of the hydrogen atoms of the methyl group.


35°
7
15 3
67°
15 1
76°
C 7
53°
C 15
51°
78°
C 6
C 8
15 2

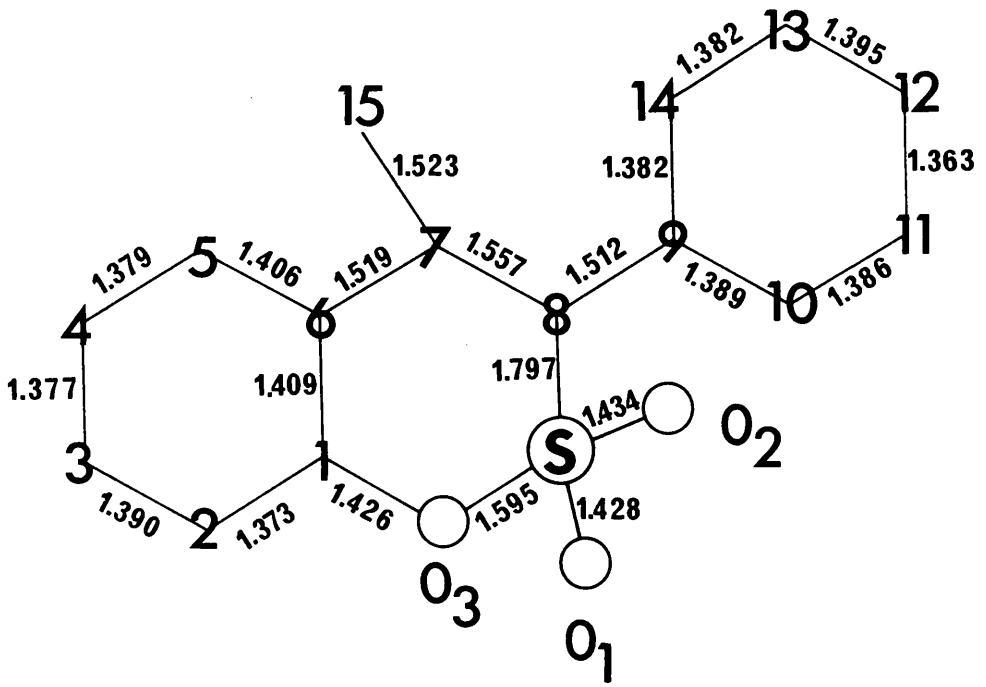
The C-H bond lengths vary from 0.86 to 1.02 Å with a mean value of 0.97 ± 0.03 Å for C_{sp^3}-H and 0.95 ± 0.02 Å for C_{sp^2}-H. From a survey of C-H bond lengths from several accurate structure determinations by X-ray methods (Stewart, Davidson, and Simpson, 1965) the mean values of 1.042 Å for C_{sp^3}-H bonds (from 69 bond lengths) and of 0.988 Å for C_{sp^2}-H bonds (from 46 bond lengths) were derived. The results from sultone B agree with these mean values. One should, however, bear in mind that the C-H bond lengths derived from X-ray analyses are shorter than those obtained by neutron diffraction or spectroscopic methods. This is because the position of an atom determined by X-ray analysis is assumed to be at the centre of the electron density. In L-ascorbic acid (Hvoslef, 1968) the C-H bonds were found to be 0.09 Å shorter from X-ray diffraction than from neutron diffraction.

The corrected bond lengths and angles of sultone B are shown in Figure 1.6. A recent structure analysis of o-hydroxyphenylethanesulphonic acid sultone (IV) (Fleischer, Kaiser, Langford, Hawkinson, Stone, and Dewar, 1967) provides an interesting comparison of its molecular dimensions (Figure 1.7) with those of sultone B. Unfortunately, the structure of IV was determined with very limited data (fewer than 20% of the reflexions accessible within the Cu

Figure 1.6

a) The bond lengths (corrected) in sultone B.

b) The bond angles (corrected) in sultone B.


15
1.523
14
1.382
13
1.382
1.395
12
1.363
11
1.386
10
1.389
9
1.512
7
1.557
1.519
5
1.406
1.379
4
6
8
1.377
1.409
1.797
3
1
S
1.434
O2
1.390
2
1.373
1.426
1.595
1.428
O3
O1

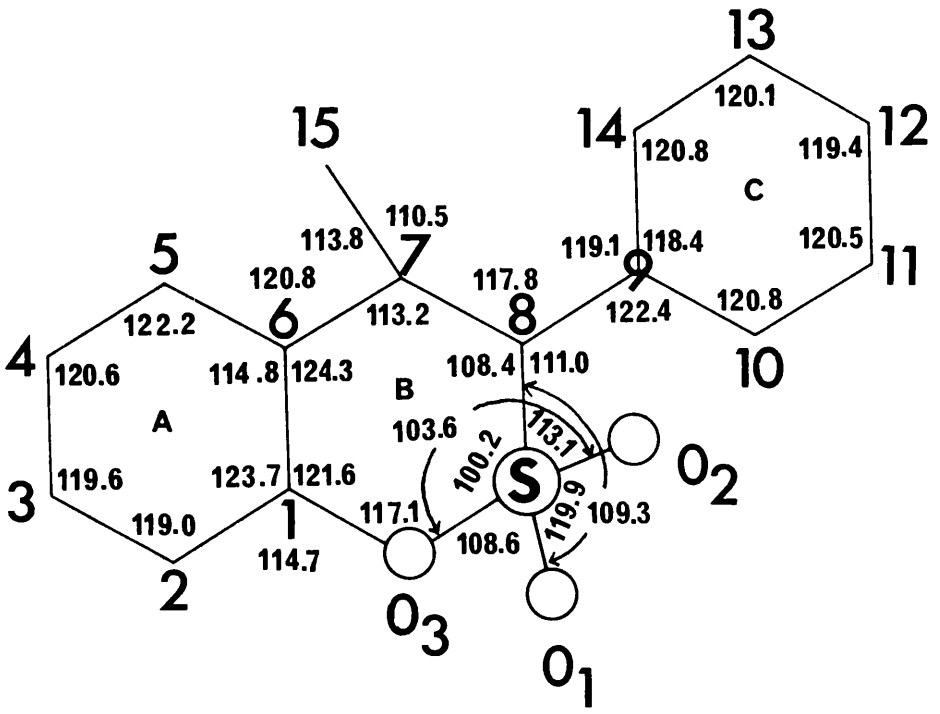
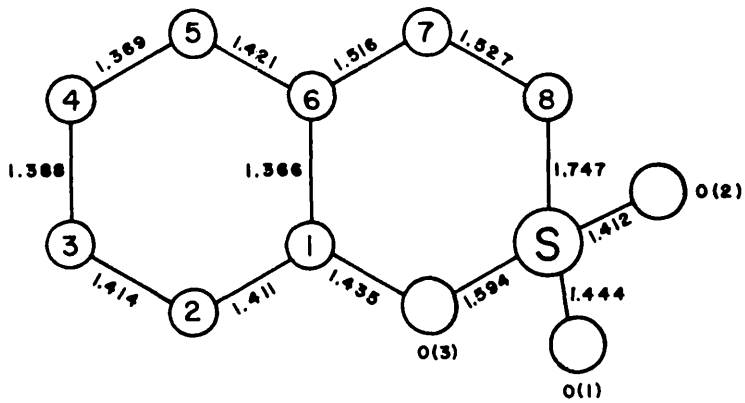
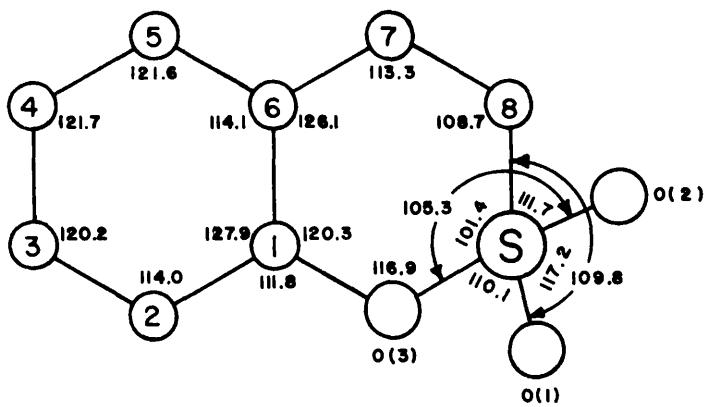
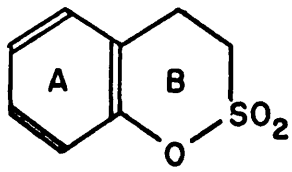

13
120.1
15
14
120.8
119.4
12
C
110.5
113.8
7
119.1
118.4
120.5
5
9
11
120.8
117.8
120.8
122.2
6
113.2
8
122.4
4
120.6
114 .8
124.3
108.4
111.0
10
B
A
103.6
113.1
100.2
O2
3
119.6
123.7
121.6
S
119.9
109.3
119.0
1
117.1
108.6
114.7
2
O3
O1

Figure 1.7

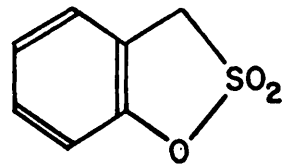
Bond lengths and angles of o-hydroxyphenylethane-sulphonic acid sultone (IV).


5
7
4
6
8
1.369
1.421
1.516
1.527
1.388
1.366
1.747
O(2)
3
1
S
1.412
1.414
2
1.411
1.435
1.594
1.444
O(3)
O(1)


5
7
121.6
113.3
4
6
8
121.7
114.1
126.1
108.7
O(2)
105.3
111.7
101.4
3
120.2
127.9
1
120.3
S
114.0
116.9
110.1
117.2
109.8
2
111.8
O(3)
O(1)



IV



V

sphere were used) and the precision claimed by the authors (e.s.d.'s of 0.009 - 0.015 Å in S-O and S-C bonds, 0.019 - 0.022 Å in C-O and C-C bonds, and approx. 1° in bond angles) appears optimistic. The same authors also determined the structure of o-hydroxy-α-toluenesulphonic acid sultone (V). The C(1)-O(3) bond lengths in the three sultones are equal within experimental errors. They are considerably longer than the C_{sp^2}-O bonds of 1.362 ± 0.001 Å in furan (Bak, Christensen, Dixon, Hansen-Nygaard, Anderson, and Schottländer, 1962) and 1.368 ± 0.008 Å in 2,4,6-trinitrophenetole (Gramaccioli, Destro, and Simonetta, 1968) in which there is no contribution from resonance and hence no double bond character. The C(1)-O(3) bond in sultone B is in fact very close to the C_{sp^3}-O bond length (1.426 ± 0.005 Å) given by Sutton (1965).

The bond lengths and valency angles associated with the sulphur atom in V and in some related molecules are listed in Table 1.12 for comparison with sultone B.

TABLE 1.12

SOME BOND LENGTHS AND VALENCY ANGLES IN SULTONE B COMPARED WITH VALUES IN RELATED COMPOUNDS

Feature in sultone B		Compared with		in	Ref.
O(1)=S=O(2)	119.9±0.2°	O=S=O	119.3±0.9°	$(CH_3SO_2)_3CH$	a
			120.4±0.4	$(p\text{-}Cl.C_6H_4)_2SO_2$	b
			118.9±1.0	V	c
			126.1±0.7	S_3O_9	d
O(3)-S=O(1)	108.6±0.2	O-S=O*	110.6±0.5	S_3O_9	
O(3)-S=O(2)	103.6±0.2	O-S=O†	103.7±0.5	S_3O_9	
		O-S=O	106.0,108.5, 101.5 (±0.4)	$KSO_4.C_2H_5$	e
			107.7,106.8 (±1.0)	V	
C(8)-S=O(1)	109.3±0.2	C-S=O	107,106,107, 111 (±1)	$(CH_3SO_2)_3CH$	
C(8)-S=O(2)	113.1±0.2		107.3,108.0 (±0.3)	$(p\text{-}Cl.C_6H_4)_2SO_2$	
			110.2,114.2 (±1.0)	V	
C(1)-O(3)-S	117.1±0.3	C-O-S	115.3±0.6	$KSO_4C_2H_5$	
S=O(1)	1.428±0.004Å	S=O	1.434±0.010Å	$(CH_3SO_2)_3CH$	
S=O(2)	1.434±0.004		1.432±0.005	$(p\text{-}Cl.C_6H_4)_2SO_2$	
			1.421,1.411 (±0.008)	V	
			1.430,1.371 (±0.013)	S_3O_9	
S-O(3)	1.595±0.004	S-O	1.604±0.004	$KSO_4C_2H_5$	
			1.627±0.008	V	
			1.626±0.007	S_3O_9	
S-C(8)	1.797±0.005	S-C_{sp^3}	1.83±0.01	$(CH_3SO_2)_3CH$	
			1.73±0.02		
			1.75±0.02	$\beta\text{-}CH_3.C_4H_5SO_2$	f
			1.80±0.02	$(CH_3)_2SO_2$	f
			1.791±0.011	V	

a Silverton, Gibson, and Abrahams, 1965
b Sime and Abrahams, 1960
c Fleischer, Kaiser, Langford, Hawkinson, Stone, and Dewar, 1967
d McDonald and Cruickshank, 1967
e Truter, 1958
f Abrahams, 1956
* axial
† equatorial

The S=O(1) and S=O(2) bond lengths are equal within experimental error and their mean value is 1.431 ± 0.003 Å. The S-O(3) bond is shorter than the formal S-O single bond (1.69 Å) and from the linear relationship between bond length and π-bond order (Cruickshank, 1961b) it has a π-bond order of about 0.25 (the same as in potassium ethyl sulphate). Various values can be found in the literature for the S-C bond length in molecules in which the sulphur atom is bonded to four other atoms. As can be seen from Table 1.12 they range from 1.73 ± 0.02 to 1.83 ± 0.01 Å. Since these values were determined with a precision lower than that of the S-C(8) bond in sultone B and one of the bonds may be of a different type, a direct comparison is therefore difficult. However, it seems reasonable to assume that the value 1.797 ± 0.005 Å is normal for this type of bond.

The atoms around the sulphur atom are arranged in a distorted tetrahedron with angles ranging from 100 to 120°. In spite of the limitations in the structure analysis of the sultone IV it is remarkable that all corresponding angles agree with each other. This includes a significant difference between the angles O(3)-S=O(1) (axial) and O(3)-S=O(2) (equatorial). In both structures the oxygen O(2) seems to be bent towards the ring oxygen O(3). Con-

sequently the angle C(8)-S=O(2) (equatorial) is larger than C(8)-S=O(1) (axial) even though not significantly so in the case of sultone IV. As a result of this bending in sultone B the non-bonded distance O(2)...O(3) (2.383 Å) is shorter than O(1)...O(3) (2.456 Å), the latter being close to the O(1)...O(2) distance (2.477 Å). These non-bonded distances are very close to the corresponding mean values in S_3O_9, viz. O (equatorial)...O (ring) of 2.39 Å, O (axial)...O (ring) of 2.46 Å, and O (axial)...O (equatorial) of 2.49 Å (McDonald and Cruickshank, 1967). In the same compound the O-S=O (axial) and O-S=O (equatorial) angles are also significantly different from each other and each of them is very close to the value found in sultone B (Table 1.12).

In the heterocyclic ring there are several significant deviations in angles from normal values, viz. at C(1), C(6), and C(7). These deviations appear to be due to the strain associated with the six-membered ring system of a sultone. This assumption is supported by the similarity of these abnormal angles to those found in sultone IV.

As mentioned earlier, there is some repulsion between the methyl group C(15) and the phenyl ring C. This is indicated by the abnormally large angle C(7)-C(8)-C(9) which deviates by 26σ from the tetrahedral value.

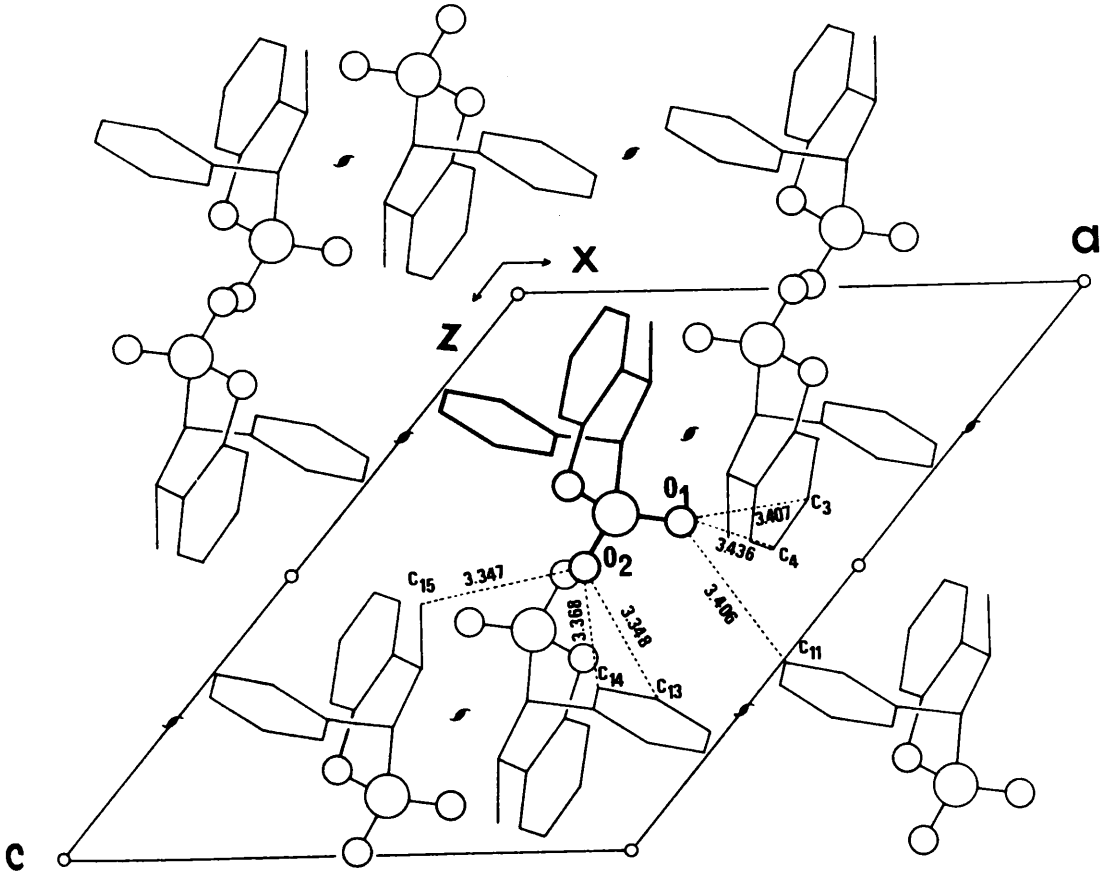
The C-C-H angles vary from 112 to 128° with a mean value of 120° in the aromatic part and from 95 to 119° with an average of 108° for the tetrahedrally arranged hydrogen atoms. None of these angles deviates significantly from normal values.

8. Intermolecular distances

The twelve contacts shorter than 3.5 Å which each molecule makes with seven neighbouring ones (Figure 1.8) are listed in Table 1.10,b); there are fifty contacts shorter than 4.0 Å with fourteen neighbouring molecules. Three of the oxygen-carbon contacts, O(2)...C(15), O(2)...C(13), and O(2)...C(14) (3.347, 3.348, and 3.368 Å), are somewhat shorter than the oxygen-carbon van der Waals distance (3.4 Å). Because of the nature of these carbon atoms no hydrogen bonds are possible and it is unlikely that these discrepancies are meaningful.

Figure 1.8

A packing diagram projected on (010). Contacts shorter than 3.5 Å are marked.


a
X
Z
c
O1
O2
C3
C4
C11
C13
C14
C15
3.401
3.436
3.406
3.347
3.368
3.348

CHAPTER II

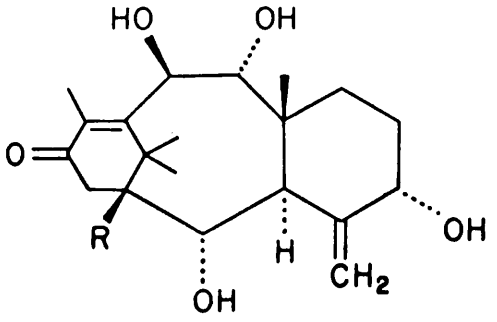
The Crystal Structure of the p-Bromobenzoate of a Dihydro-anhydro-acetonide Derivative of Taxa-4(16), 11-diene-5α, 9α, 10β, 13α-tetraol

1. Introduction

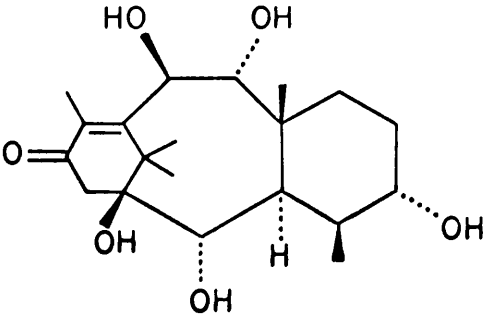
The yew, *Taxus baccata* L., is one of the major poisonous plants of Europe. The poisonous effect is undoubtedly due to a mixture of alkaloids (taxines). The major taxines, extracted from yew leaves, were shown to be esters of β-dimethylamino-β-phenylpropionic acid (Baxter, Lythgoe, Scales, Scrowston, and Trippett, 1962). Elimination of dimethylamine yielded a mixture of O-cinnamoylesters, the hydroxylic portions of which were named taxicins. Chemical and spectral studies of O-cinnamoyltaxicin-I and -II and a triacetate of the latter were carried out (Langley, Lythgoe, Scales, Scrowston, Trippett, and Wray, 1962; Eyre, Harrison, Scrowston, and Lythgoe, 1963; and Dukes, Eyre, Harrison, and Lythgoe, 1965) and it was shown that taxicin-I (structure I) and -II (structure II) are stereochemically as well as structurally analogous. Dukes *et al* (1965) also reported that the structure of 4,16-dihydrotaxicin-I is III. Independently of this work an X-ray analysis of a constituent of the leaves of Japanese yew, *Taxus cuspitata*, Sieb. et Zucc., *Taxaceae*, O-cinnamoyltaxicin-II triacetate (taxinine)

showed the structure to be IV (Shiro, Sato, Koyama, Maki, Nakanishi, and Uyeo, 1966) in agreement with the results of Dukes *et al* (1965). These substances belong to a new type of diterpenoid and the name "taxane" has been proposed for their skeleton (V) (Lythgoe, Nakanishi, and Uyeo, 1964).

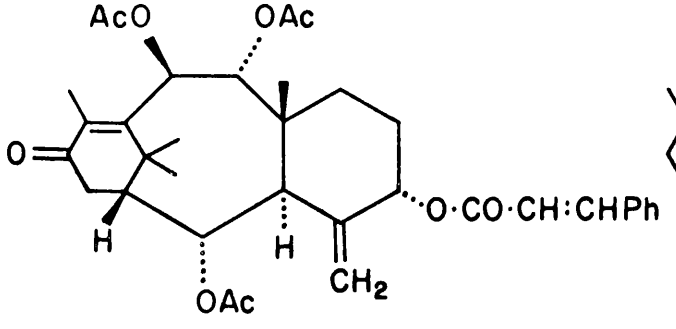
The constituents of yew heartwood (*Taxus baccata* L.) have been examined by Dr. T. G. Halsall and his coworkers in Oxford and among several compounds isolated was a new diterpene, taxadienetetraol $C_{20}H_{32}O_4$ (Chan, Halsall, Hornby, Oxford, Sabel, Bjåmer, Ferguson, and Robertson, 1966). In order to establish the structure of this compound a derivative suitable for an X-ray analysis was prepared. The tetraol was first hydrogenated and then treated with acetone and a few drops of perchloric acid. This dihydro-anhydro-acetonide was characterised as a p-bromobenzoate, m.p. 143-145°C. The latter derivative was used in this X-ray crystal structure determination. Its structure and absolute configuration were found to be as shown in VI (Bjåmer, Ferguson, and Robertson, 1967). The dihydro-anhydro-acetonide thus has the structure VII. The formation of the acetonide was known to have been accompanied by a rearrangement of the skeleton. However, the result of this rearrangement could not be elucidated.



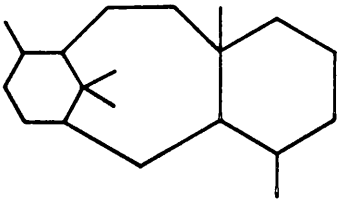
I; R = OH
II; R = H



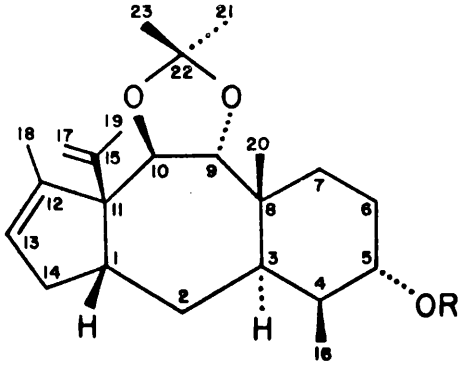
III



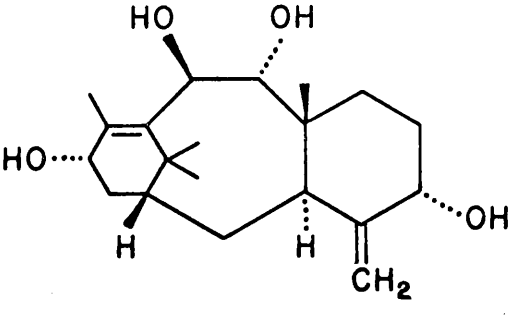
IV



V



VI; R = p – $BrC_6H_4 \cdot CO$
VII; R = H



VIII

Structure VII was unexpected since the infrared spectrum did not show a band indicative of a $=CH_2$ group. The rearrangement and its mechanism were explained on the basis of this X-ray analysis of structure VI. The taxane structure VIII was assigned to the original tetraol.

2. Crystal data

p-Bromobenzoate of a dihydro-anhydro-acetonide derivative of taxa-4(16), 11-diene-5α, 9α, 10β, 13α-tetraol, $C_{30}H_{39}O_4Br$, F.W. = 543.5, m.p. = 143-145°C. Orthorhombic, a = 17.48 ± 0.03, b = 20.62 ± 0.04, c = 7.76 ± 0.02 Å. V = 2797 ± 9 Å^3. D_m = 1.28 g.cm.$^{-3}$ (by flotation in aqueous potassium iodide), Z = 4, D_x = 1.29 g.cm.$^{-3}$. F(000) = 1144. Space group $P2_12_12_1$ (No. 19) from systematic absences. Linear absorption coefficient μ = 24.4 cm.$^{-1}$ for Cu Kα radiation (λ = 1.5418 Å).

3. Crystallographic measurements

The taxadienetetraol derivative crystallises in the shape of colourless square prisms with (010) and (100) as the predominant faces. The crystals showed sharp extinction parallel to the longest direction, [001], when examined under a polarising microscope. They are stable in the air as well as in the X-ray beam.

Oscillation, Weissenberg, and precession photographs were taken with Cu Kα (λ = 1.5418 Å) radiation from a crystal mounted along the [001] direction. The unit-cell parameters were derived from the precession photographs by taking weighted averages from the individual measurements. Correction for film shrinkage was applied and an accuracy of 2×10^{-3} in the cell parameters was assumed (Patterson and Love, 1960). The space group was determined from the systematic absences (h00 absent if h is odd, 0k0 absent if k is odd, and 00ℓ absent if ℓ is odd). Three-dimensional intensity data were obtained using a non-integrating equi-inclination Weissenberg camera with the multiple-film technique (Robertson, 1943) and the layers h0ℓ through h6ℓ were recorded. The intensities were measured visually with a calibrated intensity strip. Both hkℓ and h$\bar{k}\ell$ reflexions were measured in order to determine the absolute configuration. Out of a possible 3195 reflexions within the Cu sphere 1578 hkℓ reflexions were observed as well as 1145 h$\bar{k}\ell$ reflexions. The size of the crystal was 0.15 × 0.15 × 0.50 mm. and no absorption correction was made since μR has the low value of 0.18. The intensities were corrected for Lorentz and polarisation factors. In the early stage of the structure determination the structure factors were put on an

approximately absolute scale by making $k \sum_{hk\ell} |F_o| = \sum_{hk\ell} |F_c|$ for each layer. Unobserved reflexions were not included in any of the calculations.

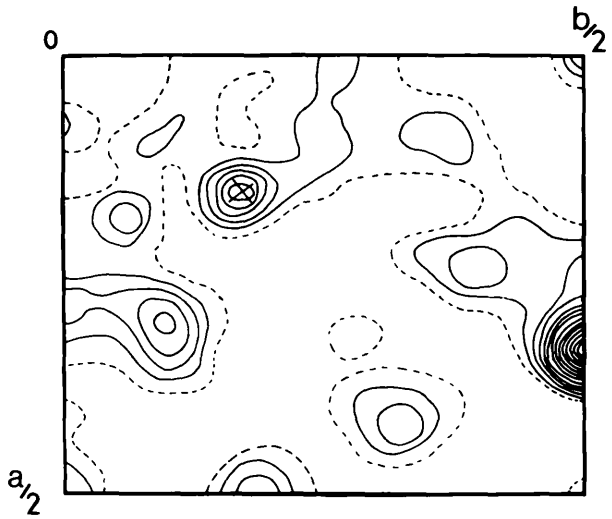
4. Structure determination

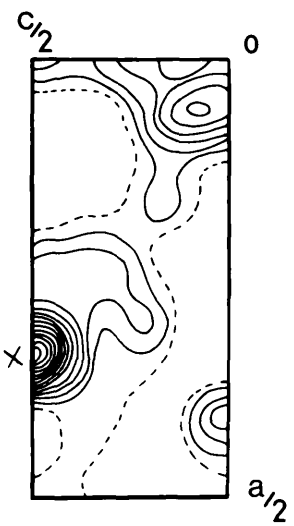
The structure was solved by the heavy-atom method ($\sum_H f_H^2 / \sum_L f_L^2 = 0.89$ at $\sin\theta = 0$). The 1578 $hk\ell$ reflexions were used in the structure determination and the 1145 $h\bar{k}\ell$ reflexions were added in the anisotropic least-squares refinement.

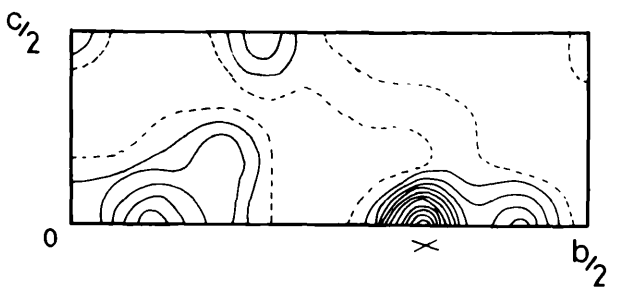
The symmetry of the Patterson vector distribution is Pmmm. In space group $P2_12_12_1$ the four equivalent positions are (x,y,z), $(\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$, $(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$, and $(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$. The Patterson map will thus contain vector peaks at $(\frac{1}{2},\frac{1}{2}+2y,2z)$, $(2x,\frac{1}{2},\frac{1}{2}+2z)$, and $(\frac{1}{2}+2x,2y,\frac{1}{2})$ from symmetry-related atoms, each with double weight. The data were sharpened to point atom with respect to bromine and the three Harker sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $w = \frac{1}{2}$ were computed. They are shown in Figure 2.1 and the three peaks interpreted as being Br-Br vector peaks are marked with a cross. The coordinates of the bromine atom, derived from these peaks by Booth's (1948b) interpolation method, were $x = 0.6700$, $y = 0.4164$, $z = 0$. With $z = 0$ the bromine peaks in the Harker sections $u = \frac{1}{2}$ and $v = \frac{1}{2}$

Figure 2.1

The three Harker sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$, and $w = \frac{1}{2}$. Contours are drawn at arbitrary intervals.


0
b/2
a/2


c/2
0
X
a/2


c/2
0
X
b/2

have four-fold weight instead of two-fold. This agreed with the observed peak heights.

A structure-factor calculation with the bromine atom in the above position gave an R-factor of 63%. With $z_{Br} = 0$ the first electron-density map based on bromine phase angles and observed amplitudes contained pseudo-mirror planes at $z = 0, \frac{1}{2}$, etc. It was possible to discern most of the atoms from this map, but the ambiguity caused by the pseudo symmetry prevented inclusion of many of them at this stage. However, the phenyl ring was clearly off the pseudo-mirror plane and was included in the second structure-factor calculation, which reduced R to 56%. In the following Fourier map there was no longer complete pseudo symmetry and the orientation of a six-membered ring was found. This ring was included as well as an oxygen of the p-bromobenzoate group in the third structure-factor calculation, which lowered R to 50%. Three further rounds of structure-factor and electron-density calculations allowed the remaining atoms to be included. At this point R was 33%. (Carbon atom C(18) was the last atom to be included since it was related to carbon atom C(12) by a pseudo-mirror plane.) In these structure-factor calculations an overall isotropic temperature parameter of $U_{iso} = 0.05$ Å^2 was used.

5. Structure refinement

Positional and thermal-vibration parameters as well as layer-scale factors were refined by least-squares methods using the block-diagonal approximation. The function minimised was $R = \sum_{hk\ell} w(|F_o| - |F_c|)^2$.

The isotropic refinement converged after five cycles of least squares, R being 15.5%. Refinement was then continued with anisotropic temperature parameters. The 1145 $h\bar{k}\ell$ reflexions were added at this stage and corrections for the real and imaginary parts of anomalous dispersion of bromine and oxygen were applied. At first, layer-scale factors were refined, but they were observed to oscillate together with the U_{ij}'s. Therefore the data were put on a common absolute scale using the layer-scale factors obtained at the end of the isotropic refinement. The anisotropic refinement was continued with one overall scale factor and it reached convergence at R = 11.7%. At this point a difference Fourier synthesis was computed and 21 of the 39 hydrogen atoms were located on peaks with heights of about 0.30 $e\text{Å}^{-3}$; the remaining 18 were in diffuse positive regions and their coordinates were calculated from geometrical considerations. The hydrogen atoms were included but their parameters were not refined in the

subsequent least-squares cycles. Their assumed temperature factors were those of the appropriate carbon atoms at the conclusion of the isotropic refinement. The average value of the parameter shifts in the last cycle was 0.2σ and the largest shift was 0.7σ. At the end of the refinement R was 10.5% and R' was 0.0215. A summary of the least-squares refinement is shown below. ($R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = \Sigma w\Delta^2/\Sigma wF_o^2$)

Cycle No.	R	R'	No. of reflexions	Parameters refined
1	0.280		1578	x,y,z, U_{iso} for Br, O, C + layer-scale factors
2	0.203		"	
3	0.174		"	
4	0.160		"	
5	0.155		"	
6	0.158	0.0348	2723	x,y,z, U_{ij} (i,j = 1,2,3) for Br, O, C + layer-scale factors
7*	0.124	0.0292	"	
8	0.117	0.0250	"	
9	0.121	0.0246	"	x,y,z, U_{ij} (i,j = 1,2,3) for Br, O, C + one overall scale factor
10*	0.116	0.0281	"	
11	0.117	0.0275	"	
12	0.113	0.0267	"	as above; hydrogen atoms included but not refined
13	0.111	0.0240	"	
14	0.107	0.0226	"	
15	0.106	0.0219	"	
16	0.105	0.0215	"	
17	0.105	0.0215	"	(structure factors only)

*Adjustments in the parameters of the weighting scheme were made.

The shift factor used in each cycle was 0.8 and the weighting scheme was: $w = (p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{-1}$. The values of the parameters p_1, p_2, and p_3 were adjusted during the refinement in order to minimise the variation of $w\Delta^2$ as a function of $|F_o|$. Initially the p_3 term was set at zero. The final values, $p_1 = 5.0$, $p_2 = 0.1$, $p_3 = 0.0002$, gave the following analysis of averaged $w\Delta^2$ as a function of $|F_o|$ and of $\sin\theta/\lambda$ at the end of the refinement:

$\|F_o\|$	$\langle w\Delta^2 \rangle$	No. of reflexions	$\sin\theta/\lambda$	$\langle w\Delta^2 \rangle$	No. of reflexions
0- 18	0.088	2019	0.0-0.2	0.105	179
18- 36	0.080	407	0.2-0.4	0.087	1247
36- 71	0.091	219	0.4-0.6	0.086	1280
71-143	0.110	69	0.6-0.8	0.080	16
143-285	0.127	8			

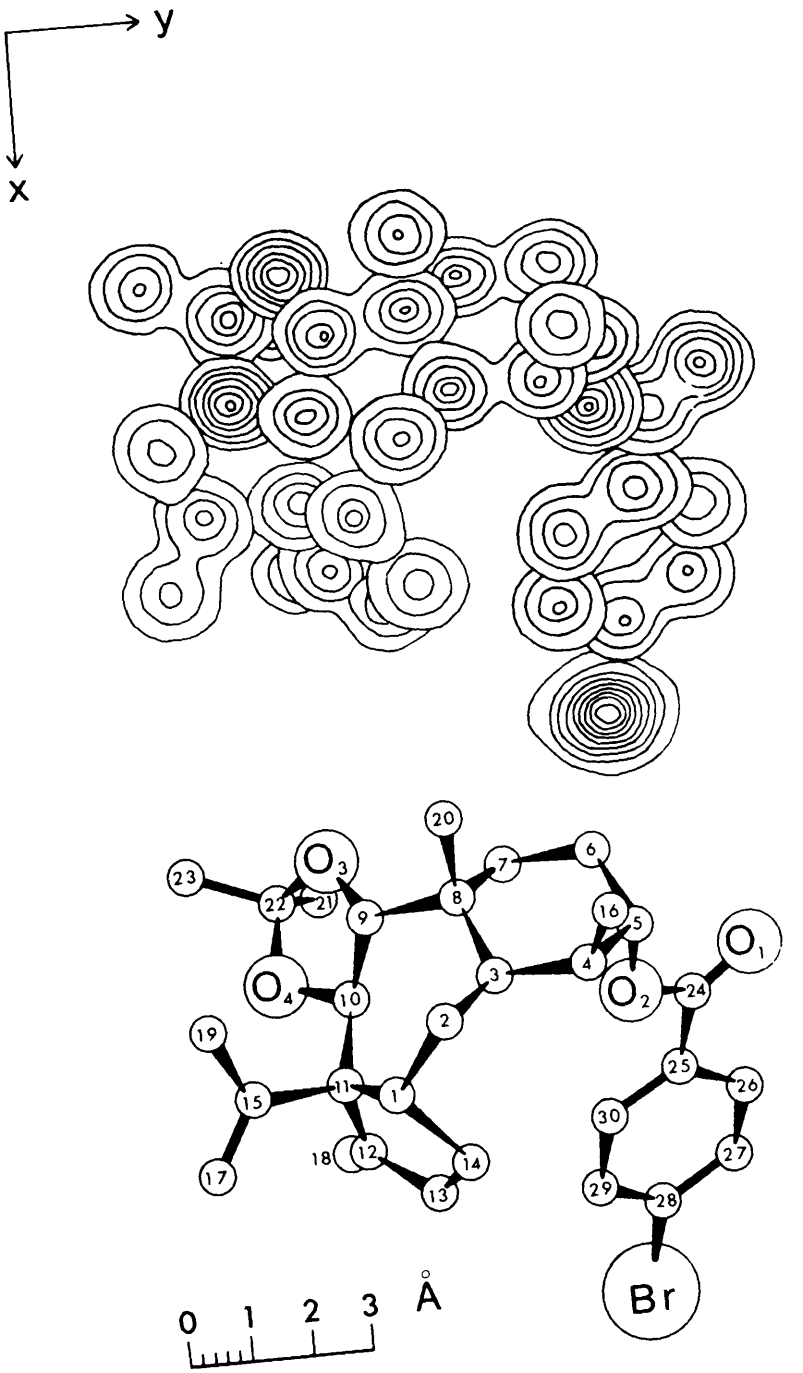
As can be seen there is little variation in $\langle w\Delta^2 \rangle$.

At the conclusion of the refinement a three-dimensional electron-density map was calculated. The composite map and its interpretation together with the numbering scheme of non-hydrogen atoms are shown in Figure 2.2. The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

The corrections for anomalous dispersion by bromine and oxygen, and the atomic scattering factors were taken

Figure 2.2

Composite three-dimensional electron-density map, viewed along the c-axis, and its interpretation with the numbering scheme. The contours start at 1 $e\mathring{A}^{-3}$ and are drawn at intervals of 1 $e\mathring{A}^{-3}$ except around the bromine atom where the intervals are 3 $e\mathring{A}^{-3}$.


y
x
O3
O4
O1
O2
Br
Å
0 1 2 3

from International Tables for X-Ray Crystallography (1962) except the scattering factors for bonded hydrogen atoms which were those of Stewart, Davidson, and Simpson (1965).

The final fractional coordinates for non-hydrogen atoms, their anisotropic temperature parameters, and fractional coordinates for hydrogen atoms with isotropic temperature factors are listed in Tables 2.1, 2.2, and 2.3, respectively. Their e.s.d.'s were derived from the inverse of the least-squares matrix. The values of the observed and calculated structure amplitudes are given in Table 2.4. Atomic coordinates, in Å, are shown in Table 2.5, and the principal values of the vibration tensors with their direction cosines in Table 2.6. Tables 2.7 and 2.8 list molecular dimensions with e.s.d.'s and non-bonded distances, respectively.

TABLE 2.1

FRACTIONAL COORDINATES AND E.S.D.s

ATOM	x/a	y/b	z/c
C(1)	0.4643 ± 6	0.2327 ± 6	0.8769 ± 15
C(2)	0.4011 ± 5	0.2753 ± 5	0.9536 ± 13
C(3)	0.3609 ± 5	0.3174 ± 5	0.8203 ± 13
C(4)	0.3563 ± 6	0.3898 ± 6	0.8708 ± 16
C(5)	0.3262 ± 5	0.4272 ± 5	0.7267 ± 14
C(6)	0.2543 ± 5	0.3982 ± 5	0.6297 ± 15
C(7)	0.2585 ± 5	0.3285 ± 5	0.6027 ± 14
C(8)	0.2831 ± 5	0.2891 ± 5	0.7564 ± 13
C(9)	0.2968 ± 5	0.2201 ± 5	0.7142 ± 13
C(10)	0.3737 ± 5	0.2041 ± 5	0.6132 ± 14
C(11)	0.4499 ± 5	0.1930 ± 4	0.7173 ± 16
C(12)	0.5147 ± 5	0.2083 ± 6	0.5938 ± 19
C(13)	0.5567 ± 6	0.2568 ± 7	0.6469 ± 20
C(14)	0.5326 ± 7	0.2828 ± 7	0.8246 ± 17
C(15)	0.4591 ± 6	0.1199 ± 5	0.7635 ± 19
C(16)	0.3101 ± 8	0.4073 ± 6	1.0297 ± 14
C(17)	0.5237 ± 8	0.0859 ± 7	0.7357 ± 24
C(18)	0.5167 ± 7	0.1955 ± 8	0.3989 ± 20
C(19)	0.3957 ± 9	0.0888 ± 7	0.8633 ± 22
C(20)	0.2141 ± 5	0.2887 ± 6	0.8887 ± 15

C(21)	0.2749 ± 6	0.1853 ± 7	0.2932 ± 15
C(22)	0.2769 ± 5	0.1539 ± 5	0.4767 ± 14
C(23)	0.2456 ± 7	0.0843 ± 6	0.4763 ± 18
C(24)	0.3924 ± 5	0.4698 ± 6	0.4710 ± 16
C(25)	0.4626 ± 6	0.4551 ± 5	0.3553 ± 15
C(26)	0.4865 ± 7	0.5039 ± 6	0.2307 ± 22
C(27)	0.5457 ± 7	0.4900 ± 6	0.1317 ± 16
C(28)	0.5843 ± 6	0.4336 ± 5	0.1355 ± 15
C(29)	0.5648 ± 8	0.3853 ± 6	0.2457 ± 23
C(30)	0.5024 ± 6	0.3961 ± 5	0.3649 ± 14
O(1)	0.3515 ± 4	0.5164 ± 4	0.4608 ± 12
O(2)	0.3886 ± 4	0.4219 ± 3	0.5886 ± 11
O(3)	0.2423 ± 3	0.1925 ± 3	0.6041 ± 10
O(4)	0.3552 ± 3	0.1467 ± 3	0.5231 ± 10
Br(1)	0.6680 ± 1	0.4176 ± 1	-0.0055 ± 2

TABLE 2.2

ANISOTROPIC TEMPERATURE PARAMETERS AND E.S.D.s (A^{o2})

ATOM	U 11	U 22	U 33	2U 23	2U 31	2U 12
C(1)	0.0871	0.1431	0.0805	0.0164	-0.0052	0.0300
	62	92	74	136	118	124
C(2)	0.0737	0.0952	0.0863	-0.0069	-0.0336	0.0153
	50	60	76	107	92	88
C(3)	0.0658	0.0991	0.0790	0.0076	-0.0088	0.0167
	46	64	67	102	88	86
C(4)	0.0737	0.1157	0.1072	-0.0021	-0.0127	-0.0198
	54	76	88	128	113	100
C(5)	0.0714	0.0919	0.1065	0.0101	0.0240	0.0332
	51	60	77	114	106	97
C(6)	0.0584	0.1149	0.0933	0.0258	0.0054	0.0117
	43	73	79	115	95	89
C(7)	0.0694	0.0913	0.0827	0.0165	-0.0255	0.0191
	48	59	65	100	97	84
C(8)	0.0557	0.0927	0.0815	0.0239	-0.0021	0.0027
	39	58	69	100	80	80
C(9)	0.0660	0.0975	0.0743	0.0056	0.0123	-0.0167
	46	62	66	101	86	84
C(10)	0.0711	0.0764	0.0931	-0.0022	-0.0300	-0.0076
	46	52	68	99	96	80
C(11)	0.0585	0.0790	0.1182	-0.0291	-0.0419	0.0306
	42	54	81	104	94	77
C(12)	0.0524	0.1308	0.1418	0.0046	-0.0204	0.0117
	43	84	100	154	107	100
C(13)	0.0601	0.1630	0.1391	-0.0067	0.0040	0.0058
	48	110	114	173	125	115

C(14)	0.0824	0.1659	0.1195	0.0122	-0.0696	-0.0453
	63	108	105	179	136	143
C(15)	0.0907	0.1030	0.1311	0.0194	-0.0577	0.0349
	68	74	98	140	144	112
C(16)	0.1180	0.1463	0.0637	-0.0500	-0.0133	0.0148
	79	95	74	131	118	134
C(17)	0.1223	0.1431	0.1620	-0.0167	-0.0651	0.1022
	97	104	131	207	196	169
C(18)	0.0897	0.1941	0.1199	-0.1066	0.0766	-0.0671
	70	140	103	200	144	165
C(19)	0.1458	0.1175	0.1400	0.1026	-0.0148	0.0287
	112	88	126	178	188	160
C(20)	0.0744	0.1329	0.0809	0.0459	0.0286	0.0057
	53	82	73	126	101	112
C(21)	0.0824	0.1619	0.0684	0.0257	0.0010	-0.0029
	60	102	72	130	100	130
C(22)	0.0713	0.1176	0.0781	-0.0179	-0.0351	-0.0239
	48	70	70	115	100	95
C(23)	0.1107	0.1033	0.1259	-0.0047	-0.0548	-0.0056
	78	71	106	155	154	112
C(24)	0.0747	0.1369	0.0974	0.0291	-0.0217	-0.0018
	54	85	88	150	113	109
C(25)	0.0746	0.1045	0.1059	0.0005	-0.0075	0.0007
	52	71	85	122	113	98
C(26)	0.1025	0.1110	0.1612	0.0579	0.0165	0.0496
	79	85	121	167	162	128
C(27)	0.1129	0.1420	0.0907	0.0459	0.0254	0.0011
	83	101	84	148	148	145
C(28)	0.0996	0.0975	0.0924	-0.0159	0.0614	-0.0083
	66	67	81	118	121	108
C(29)	0.1057	0.0973	0.1573	-0.0157	0.0212	0.0266
	79	72	119	155	171	123

C(30)	0.1051	0.0876	0.0817	0.0043	0.0309	0.0114
	70	58	74	104	118	102
O(1)	0.1101	0.1107	0.1349	0.0458	0.0395	0.0819
	52	50	69	98	98	85
O(2)	0.0745	0.0835	0.1247	0.0262	0.0315	0.0227
	36	38	55	76	72	61
O(3)	0.0596	0.1006	0.1003	-0.0189	0.0222	0.0028
	29	43	49	74	64	58
O(4)	0.0691	0.1008	0.1041	-0.0014	0.0116	0.0197
	32	42	51	80	72	59
Br(1)	0.1222	0.1375	0.1339	-0.0213	0.0872	-0.0216
	10	10	12	20	21	16

TABLE 2.3

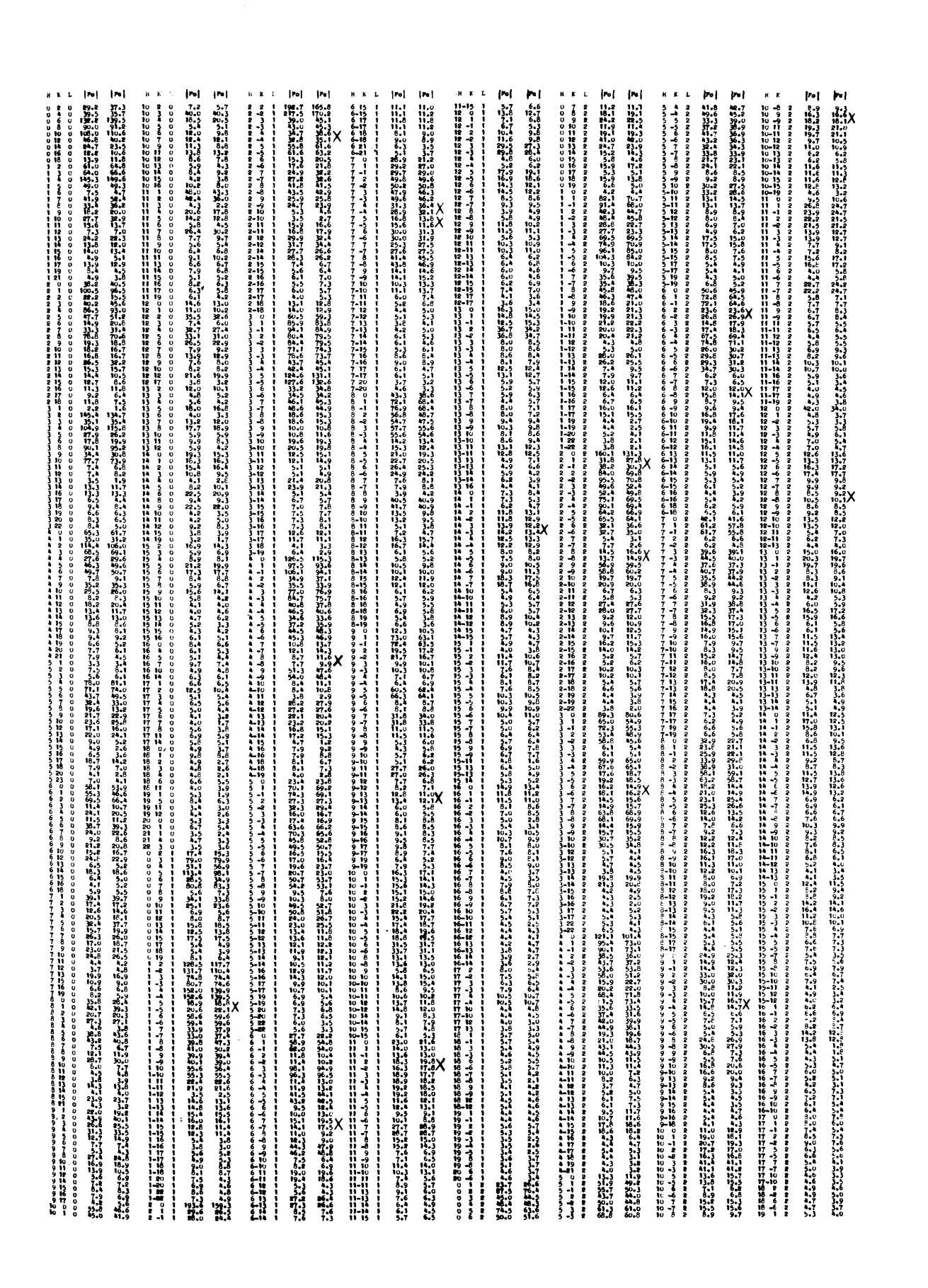
HYDROGEN-ATOM FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE PARAMETERS

ATOM	x/a	y/b	z/c	U (A^2)
H(1)	0.474	0.199	0.976	0.117
H(2)	0.359	0.243	1.001	0.084
H(2)^1	0.424	0.306	1.044	0.084
H(3)^2	0.399	0.312	0.712	0.071
H(4)	0.413	0.409	0.884	0.097
H(5)	0.316	0.477	0.734	0.080
H(6)	0.214	0.406	0.719	0.077
H(6)^1	0.249	0.430	0.513	0.077
H(7)^2	0.211	0.313	0.565	0.082
H(7)^1	0.304	0.322	0.512	0.082
H(9)^2	0.292	0.204	0.848	0.075
H(10)	0.384	0.250	0.566	0.079
H(13)	0.602	0.282	0.573	0.095
H(14)	0.514	0.333	0.824	0.112
H(14)^1	0.575	0.288	0.891	0.112
H(16)^2	0.307	0.469	1.033	0.117
H(16)^1	0.243	0.406	1.023	0.117
H(16)^2	0.325	0.385	1.149	0.117
H(17)^3	0.518	0.031	0.747	0.127
H(17)^1	0.578	0.113	0.724	0.127
^{2}				

H(18)^{1}	0.474	0.160	0.412	0.109
H(18)^{2}	0.509	0.232	0.308	0.109
H(18)^{3}	0.568	0.182	0.335	0.109
H(19)^{1}	0.336	0.088	0.830	0.117
H(19)^{2}	0.409	0.042	0.887	0.117
H(19)^{3}	0.389	0.122	0.983	0.117
H(20)^{1}	0.227	0.260	0.991	0.093
H(20)^{2}	0.196	0.334	0.948	0.093
H(20)^{3}	0.160	0.267	0.881	0.093
H(21)^{1}	0.314	0.175	0.188	0.108
H(21)^{2}	0.223	0.205	0.329	0.108
H(21)^{3}	0.326	0.215	0.294	0.108
H(23)^{1}	0.266	0.048	0.417	0.101
H(23)^{2}	0.243	0.075	0.618	0.101
H(23)^{3}	0.202	0.061	0.404	0.101
H(26)	0.451	0.546	0.216	0.113
H(27)	0.566	0.528	0.046	0.104
H(29)	0.578	0.324	0.245	0.098
H(30)	0.484	0.361	0.451	0.092

TABLE 2.4

OBSERVED AND CALCULATED STRUCTURE FACTORS



H	K	L	Fo	Fc
0	0	2	1.1	1.1
0	0	4	1.1	1.1
0	0	6	1.1	1.1
0	0

TABLE 2.5

COORDINATES IN ANGSTRØM AND E.S.D.s

ATOM	X	Y	Z
C(1)	8.117 ± 11	4.799 ± 13	6.805 ± 12
C(2)	7.012 ± 9	5.676 ± 10	7.400 ± 10
C(3)	6.309 ± 9	6.546 ± 10	6.366 ± 10
C(4)	6.229 ± 10	8.038 ± 12	6.758 ± 13
C(5)	5.702 ± 9	8.808 ± 10	5.640 ± 11
C(6)	4.446 ± 9	8.210 ± 10	4.886 ± 12
C(7)	4.518 ± 9	6.774 ± 10	4.677 ± 11
C(8)	4.949 ± 8	5.961 ± 9	5.870 ± 10
C(9)	5.189 ± 8	4.539 ± 10	5.542 ± 10
C(10)	6.531 ± 8	4.208 ± 9	4.758 ± 11
C(11)	7.864 ± 8	3.979 ± 9	5.566 ± 12
C(12)	8.997 ± 9	4.295 ± 13	4.608 ± 15
C(13)	9.731 ± 10	5.295 ± 14	5.020 ± 15
C(14)	9.309 ± 12	5.832 ± 15	6.399 ± 13
C(15)	8.025 ± 11	2.473 ± 11	5.925 ± 15
C(16)	5.420 ± 13	8.398 ± 13	7.991 ± 11
C(17)	9.154 ± 15	1.772 ± 15	5.709 ± 19
C(18)	9.032 ± 12	4.032 ± 16	3.095 ± 16
C(19)	6.916 ± 16	1.831 ± 14	6.699 ± 17
C(20)	3.742 ± 9	5.953 ± 12	6.896 ± 12

C(21)	4.805 ± 11	3.821 ± 14	2.275 ± 12
C(22)	4.840 ± 9	3.174 ± 11	3.699 ± 11
C(23)	4.293 ± 12	1.738 ± 12	3.696 ± 14
C(24)	6.858 ± 9	9.688 ± 12	3.655 ± 12
C(25)	8.087 ± 10	9.384 ± 11	2.758 ± 12
C(26)	8.505 ± 12	10.390 ± 12	1.790 ± 17
C(27)	9.539 ± 13	10.103 ± 13	1.022 ± 12
C(28)	10.214 ± 11	8.940 ± 10	1.052 ± 12
C(29)	9.872 ± 13	7.945 ± 12	1.906 ± 18
C(30)	8.781 ± 11	8.167 ± 10	2.832 ± 11
O(1)	6.144 ± 8	10.649 ± 8	3.576 ± 9
O(2)	6.793 ± 6	8.700 ± 7	4.568 ± 8
O(3)	4.235 ± 6	3.970 ± 6	4.688 ± 8
O(4)	6.209 ± 6	3.025 ± 6	4.059 ± 8
Br(1)	11.676 ± 1	8.612 ± 1	-0.042 ± 2

TABLE 2.6

PRINCIPAL VALUES OF VIBRATION TENSORS AND THEIR DIRECTION COSINES REFERRED TO CRYSTAL AXES

ATOM	$U(A^{o2})$	D1	D2	D3
C(1)	0.1477	0.2346	0.9660	0.1089
	0.0767	0.5214	-0.2195	0.8246
	0.0864	0.8204	-0.1367	-0.5552
C(2)	0.0615	0.8293	-0.1326	0.5429
	0.1041	-0.4871	-0.6475	0.5860
	0.0896	0.2738	-0.7504	-0.6016
C(3)	0.1014	0.2122	0.9695	0.1227
	0.0622	0.9244	-0.2399	0.2967
	0.0803	0.3171	0.0505	-0.9470
C(4)	0.0704	0.9616	0.2140	0.1719
	0.1179	-0.2233	0.9741	0.0368
	0.1083	-0.1595	-0.0738	0.9844
C(5)	0.0607	-0.8802	0.4382	0.1821
	0.1152	0.3910	0.4523	0.8016
	0.0939	0.2689	0.7768	-0.5694
C(6)	0.1216	0.1014	0.9014	0.4209
	0.0577	-0.9948	0.0923	0.0420
	0.0873	-0.0010	-0.4230	0.9062
C(7)	0.0571	0.7917	-0.3432	0.5054
	0.0965	0.1122	0.8949	0.4319
	0.0898	-0.6005	-0.2853	0.7470
C(8)	0.1003	0.0129	0.8443	0.5358
	0.0556	0.9961	-0.0577	0.0669
	0.0740	0.0874	0.5328	-0.8417
C(9)	0.0996	-0.2318	0.9714	0.0511
	0.0607	-0.8683	-0.2303	0.4393
	0.0775	0.4385	0.0575	0.8969
C(10)	0.1007	-0.4547	0.0308	0.8901
	0.0624	0.8617	0.2681	0.4309
	0.0775	-0.2254	0.9629	-0.1484

C(11)	0.1315	-0.3245	-0.3393	0.8829
	0.0480	0.9128	-0.3570	0.1983
	0.0762	0.2479	0.8703	0.4256
C(12)	0.0508	0.9907	-0.0757	0.1129
	0.1432	-0.1021	0.1350	0.9856
	0.1310	-0.0898	-0.9880	0.1260
C(13)	0.0600	-0.9992	0.0290	0.0265
	0.1635	-0.0252	-0.9907	0.1338
	0.1387	0.0301	0.1330	0.9907
C(14)	0.0590	0.8632	0.1554	0.4804
	0.1762	-0.3270	0.8970	0.2973
	0.1327	-0.3848	-0.4137	0.8251
C(15)	0.0652	0.7831	-0.4665	0.4112
	0.1461	-0.4580	0.0146	0.8888
	0.1135	-0.4206	-0.8844	-0.2023
C(16)	0.0564	0.0725	0.2617	0.9624
	0.1554	-0.2330	-0.9338	0.2714
	0.1162	0.9698	-0.2439	-0.0067
C(17)	0.0756	0.7879	-0.5663	0.2420
	0.2038	-0.5874	-0.5729	0.5716
	0.1480	-0.1850	-0.5925	-0.7840
C(18)	0.2374	0.3101	-0.8238	0.4746
	0.0636	-0.8144	0.0273	0.5796
	0.1027	-0.4904	-0.5663	-0.6624
C(19)	0.0728	0.2120	-0.7654	0.6076
	0.1816	0.0962	0.6351	0.7664
	0.1489	-0.9725	-0.1041	0.2083
C(20)	0.1425	0.1164	0.9215	0.3704
	0.0606	-0.6847	-0.1957	0.7020
	0.0852	0.7194	-0.3354	0.6082
C(21)	0.1637	-0.0169	0.9909	0.1336
	0.0666	-0.0437	-0.1342	0.9900
	0.0824	0.9989	0.0108	0.0456
C(22)	0.0534	0.7540	0.2262	0.6167
	0.1211	0.1896	-0.9738	0.1254
	0.0926	0.6289	0.0224	-0.7771

C(23)	0.1467	-0.6051	-0.0041	0.7962
	0.0889	0.7710	0.2464	0.5872
	0.1042	-0.1986	0.9692	-0.1459
C(24)	0.1420	-0.0649	0.9438	0.3240
	0.0700	0.9128	-0.0750	0.4014
	0.0970	0.4031	0.3218	-0.8567
C(25)	0.0742	0.9930	-0.0124	0.1174
	0.1064	-0.1153	0.1106	0.9872
	0.1045	-0.0252	-0.9938	0.1084
C(26)	0.1788	0.2403	0.4540	0.8580
	0.0793	0.6884	-0.7028	0.1791
	0.1165	0.6844	0.5476	-0.4814
C(27)	0.0780	-0.3198	-0.3174	0.8928
	0.1515	0.1365	0.9170	0.3749
	0.1161	-0.9376	0.2418	-0.2499
C(28)	0.1291	0.7134	-0.2573	0.6518
	0.0648	-0.6512	0.1002	0.7523
	0.0956	-0.2589	-0.9611	-0.0961
C(29)	0.1598	0.1708	-0.0869	0.9815
	0.0853	-0.6002	0.7808	0.1736
	0.1151	-0.7814	-0.6187	0.0812
C(30)	0.1142	0.8745	0.2225	0.4309
	0.0740	-0.4514	0.0483	0.8910
	0.0862	0.1775	-0.9737	0.1427
O(1)	0.1744	0.5510	0.5724	0.6072
	0.0694	0.6990	-0.7141	0.0389
	0.1119	0.4558	0.4031	-0.7936
O(2)	0.1342	0.2963	0.3006	0.9065
	0.0660	-0.8728	0.4706	0.1293
	0.0825	-0.3878	-0.8296	0.4018
O(3)	0.0564	-0.9612	0.0865	0.2620
	0.1109	0.1418	-0.6595	0.7382
	0.0932	0.2367	0.7467	0.6217
O(4)	0.0654	-0.9520	0.2680	0.1476
	0.1054	0.2487	0.3964	0.8838
	0.1032	0.1783	0.8781	-0.4440
Br(1)	0.0840	-0.7550	-0.0219	0.6554
	0.1777	0.6194	-0.3520	0.7017
	0.1318	0.2153	0.9357	0.2794

TABLE 2.7

MOLECULAR DIMENSIONS

(a) Bond lengths and e.s.d.'s

C(1) -C(2)	1.531 ± 15 Å	C(12)-C(13)	1.307 ± 18 Å
C(2) -C(3)	1.523 ± 14	C(15)-C(17)	1.346 ± 19
C(3) -C(4)	1.545 ± 15		
C(3) -C(8)	1.561 ± 12	C(24)-C(25)	1.552 ± 15
C(4) -C(5)	1.456 ± 16		
C(5) -C(6)	1.582 ± 14	C(25)-C(26)	1.457 ± 18
C(6) -C(7)	1.453 ± 14	C(26)-C(27)	1.320 ± 19
C(7) -C(8)	1.507 ± 14	C(27)-C(28)	1.345 ± 17
C(8) -C(9)	1.479 ± 14	C(28)-C(29)	1.356 ± 18
C(9) -C(10)	1.590 ± 13	C(29)-C(30)	1.448 ± 19
C(10)-C(11)	1.575 ± 13	C(30)-C(25)	1.403 ± 15
C(11)-C(1)	1.507 ± 17		
C(1) -C(14)	1.629 ± 18	O(1) -C(24)	1.200 ± 14
C(4) -C(16)	1.518 ± 17		
C(8) -C(20)	1.584 ± 14	O(2) -C(24)	1.347 ± 15
C(21)-C(22)	1.565 ± 16		
C(22)-C(23)	1.537 ± 16	O(2) -C(5)	1.533 ± 13
		O(3) -C(9)	1.401 ± 12
C(11)-C(12)	1.517 ± 15	O(3) -C(22)	1.406 ± 12
C(12)-C(18)	1.535 ± 22	O(4) -C(10)	1.412 ± 12
C(13)-C(14)	1.538 ± 20	O(4) -C(22)	1.423 ± 11
C(15)-C(11)	1.557 ± 15		
C(15)-C(19)	1.497 ± 20	Br-C(28)	1.855 ± 11

(b) Bond angles and e.s.d.'s

C(2) -C(1) -C(11)	120.7 ± 0.9°	C(1) -C(14)-C(13)	101.7 ± 1.0°
C(2) -C(1) -C(14)	105.2 ± 1.0	C(21)-C(22)-C(23)	112.1 ± 0.9
C(11)-C(1) -C(14)	105.2 ± 0.9	C(21)-C(22)-O(3)	113.4 ± 0.9
C(1) -C(2) -C(3)	113.3 ± 0.9	C(21)-C(22)-O(4)	107.1 ± 0.8
C(2) -C(3) -C(4)	113.8 ± 0.9	C(23)-C(22)-O(3)	112.2 ± 0.8
C(2) -C(3) -C(8)	113.8 ± 0.8	C(23)-C(22)-O(4)	104.2 ± 0.8
C(4) -C(3) -C(8)	113.4 ± 0.8	O(3) -C(22)-O(4)	107.2 ± 0.8
C(3) -C(4) -C(5)	109.6 ± 1.0		
C(3) -C(4) -C(16)	117.6 ± 1.0	C(11)-C(12)-C(13)	112.3 ± 1.2
C(5) -C(4) -C(16)	107.8 ± 0.9	C(11)-C(12)-C(18)	127.2 ± 1.0
C(4) -C(5) -C(6)	117.0 ± 0.9	C(13)-C(12)-C(18)	115.4 ± 1.2
C(4) -C(5) -O(2)	104.0 ± 0.8	C(12)-C(13)-C(14)	113.3 ± 1.2
C(6) -C(5) -O(2)	101.9 ± 0.8	C(11)-C(15)-C(19)	117.2 ± 1.0
C(5) -C(6) -C(7)	113.7 ± 0.8	C(11)-C(15)-C(17)	123.6 ± 1.1
C(6) -C(7) -C(8)	115.7 ± 0.9	C(19)-C(15)-C(17)	118.7 ± 1.2
C(3) -C(8) -C(7)	107.4 ± 0.8		
C(3) -C(8) -C(9)	106.8 ± 0.7	C(25)-C(24)-O(1)	126.2 ± 1.1
C(3) -C(8) -C(20)	117.4 ± 0.8	C(25)-C(24)-O(2)	106.7 ± 0.9
C(7) -C(8) -C(9)	112.9 ± 0.8	O(1) -C(24)-O(2)	127.1 ± 1.0
C(7) -C(8) -C(20)	107.4 ± 0.7		
C(9) -C(8) -C(20)	105.2 ± 0.8	C(24)-C(25)-C(26)	118.4 ± 1.0
C(8) -C(9) -C(10)	116.5 ± 0.8	C(24)-C(25)-C(30)	122.1 ± 1.0
C(8) -C(9) -O(3)	114.6 ± 0.7	C(26)-C(25)-C(30)	119.5 ± 1.0
C(10)-C(9) -O(3)	100.9 ± 0.7	C(25)-C(26)-C(27)	117.5 ± 1.1
C(9) -C(10)-C(11)	119.5 ± 0.9	C(26)-C(27)-C(28)	124.6 ± 1.2
C(9) -C(10)-O(4)	103.1 ± 0.7	C(27)-C(28)-C(29)	121.5 ± 1.2
C(11)-C(10)-O(4)	109.0 ± 0.7	C(27)-C(28)-Br	122.4 ± 0.9
C(1) -C(11)-C(10)	119.0 ± 0.8	C(29)-C(28)-Br	116.1 ± 0.9
C(1) -C(11)-C(12)	106.3 ± 0.9	C(28)-C(29)-C(30)	118.7 ± 1.0
C(1) -C(11)-C(15)	108.6 ± 1.0	C(25)-C(30)-C(29)	118.2 ± 1.0
C(10)-C(11)-C(12)	106.1 ± 0.9		
C(10)-C(11)-C(15)	110.3 ± 0.8	C(5) -O(2) -C(24)	117.2 ± 0.7
C(12)-C(11)-C(15)	105.6 ± 0.9	C(9) -O(3) -C(22)	111.5 ± 0.7
		C(10)-O(4) -C(22)	104.9 ± 0.7

TABLE 2.8

NON-BONDED DISTANCES

(a) Some intramolecular distances

C(4) ...C(8)	2.60 Å
C(16)...C(20)	3.16
C(16)...C(5)	2.40
C(16)...C(3)	2.62
C(20)...C(9)	2.43
C(20)...C(7)	2.49
C(20)...C(3)	2.69
C(15)...O(4)	2.66
C(17)...C(12)	2.76
C(17)...C(1)	3.38
C(18)...O(4)	3.15
C(18)...C(15)	3.38
C(18)...C(17)	3.46
C(19)...O(4)	2.98
C(19)...C(10)	3.09
C(19)...C(1)	3.20
C(19)...C(9)	3.41
C(19)...C(22)	3.89
C(19)...C(23)	3.99
O(1) ...C(26)	2.97
O(2) ...C(30)	2.69

(b) Intermolecular distances <4.0Å

Atom A	Atom B	Equivalent position* of Atom B	Cell of Atom B	Distance
O(1)	...C(16)	II	(0, 0,-1)	3.28Å
O(1)	...C(17)	IV	(0, 0, 1)	3.52
O(1)	...C(6)	II	(0, 0,-1)	3.62
O(1)	...C(5)	II	(0, 0,-1)	3.78
O(2)	...C(17)	IV	(0, 0, 1)	3.96
O(3)	...C(29)	III	(-1, 0, 1)	3.68
O(3)	...C(13)	III	(-1, 0, 1)	3.93
O(4)	...C(27)	IV	(0,-1, 0)	3.86
Br	...C(21)	III	(0, 0, 0)	3.60
Br	...C(23)	IV	(0, 0, 0)	3.76
Br	...C(14)	I	(0, 0,-1)	3.88
Br	...C(23)	III	(0, 0, 0)	3.90
C(24)	...C(17)	IV	(0, 0, 1)	3.61
C(24)	...C(16)	I	(0, 0,-1)	3.93
C(25)	...C(16)	I	(0, 0,-1)	3.80
C(26)	...C(16)	I	(0, 0,-1)	3.99
C(27)	...C(17)	IV	(0, 0, 0)	3.68
C(29)	...C(23)	III	(0, 0, 1)	3.88
C(29)	...C(14)	I	(0, 0,-1)	3.93
C(2)	...C(21)	I	(0, 0, 1)	3.91
C(20)	...C(21)	I	(0, 0, 1)	3.94

*The equivalent positions are:

I (x, y, z)

II (½-x,1-y,½+z)

III (½+x,½-y, -z)

IV (1-x,½+y,½-z)

Atom A is in equivalent position I in the cell (0,0,0)

6. Absolute configuration

If there are atoms present which give rise to anomalous scattering of the X-rays, Friedel's law no longer holds and for the space group $P2_12_12_1$ we have: $I_{hk\ell} = I_{\bar{h}\bar{k}\ell} = I_{\bar{h}k\bar{\ell}} = I_{h\bar{k}\bar{\ell}} \neq I_{\bar{h}\bar{k}\bar{\ell}} = I_{\bar{h}k\ell} = I_{h\bar{k}\ell} = I_{hk\bar{\ell}}$. In this structure bromine is the anomalous scatterer. The reflexions were indexed with respect to a right-handed set of axes (Peerdeman and Bijvoet, 1956) and, as previously mentioned, all the recorded intensities of the Bijvoet pairs $hk\ell$ and $h\bar{k}\ell$ were estimated, making it possible to determine the absolute configuration (Bijvoet, 1955). The reflexions which have a difference of about 10% or more in the calculated structure factors of the Bijvoet pairs are marked with a cross in Table 2.4. There are 41 such pairs of reflexions and for 35 of them the observed structure factors show differences with the same sign as the calculated ones, two have a small difference with opposite sign and four no appreciable difference. This shows clearly that the molecule chosen is in fact the one with the correct absolute configuration and not the mirror image. The absolute configuration is seen in structure VI and Figure 2.2. (All figures are drawn with respect to a right-handed coordinate system.) As can be seen from VI the absolute configuration is in agreement with that determined for taxicin-I and -II (structures I, II) (Dukes *et al*, 1965).

7. Description and discussion of the structure

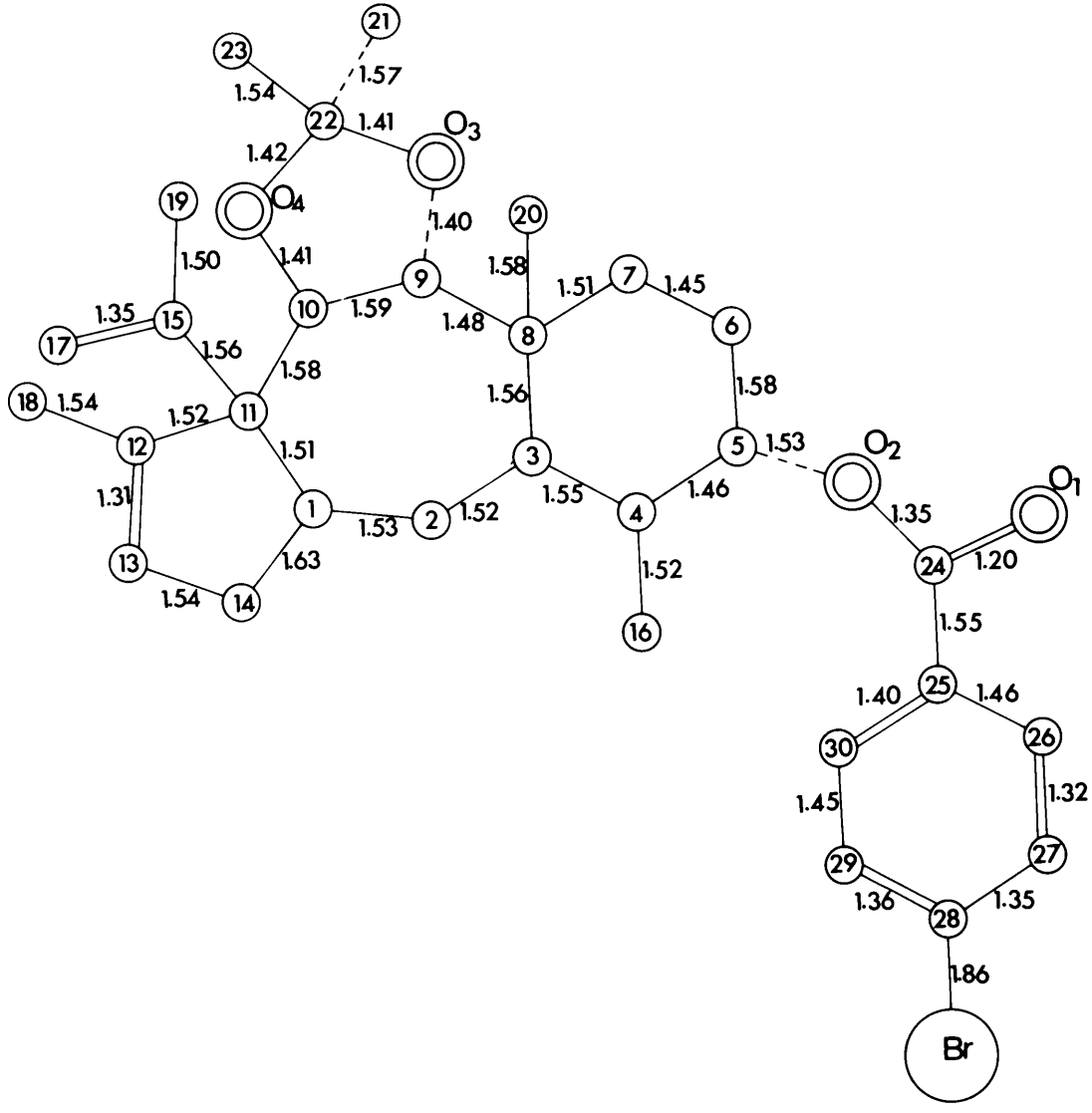
This crystal structure determination of the p-bromobenzoate of the dihydro-anhydro-acetonide derivative of taxadienetetraol shows that the rearranged tetraol part of the derivative is tricyclic with a cyclohexane, a cycloheptane, and a cyclopentene ring. The structure with bond lengths and angles is shown in Figure 2.3. The least-squares planes are listed in Table 2.9.

The cyclohexane ring, *trans*-fused with the cycloheptane ring, is in a slightly distorted chair conformation. This can be seen from the displacements of the atoms from the "best" plane through the six carbon atoms of the ring. The mean value of the displacements is 0.20 Å. (On the basis of calculations each ring atom in a cyclohexane chair, with all angles tetrahedral, is displaced from the mean plane by ± 0.26 Å.) Thus the general effect is a flattening of the ring and in particular at C(5) and C(6) which are displaced by only ± 0.14 Å. The p-bromobenzoate group as well as the two methyl carbon atoms (C(16) and C(20)) are in axial positions. The latter two atoms are bent away from each other so that repulsive forces are diminished. This can be seen by comparing the non-bonded distances C(4)...C(8) (2.60 Å) with the much

Figure 2.3

a) Bond lengths

b) Bond angles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23
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22
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O3
1.42
O4
19
1.40
20
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7
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12
3
5
1.53
O2
O1
1.51
1.31
1.55
1.46
1
1.53
2
1.52
4
1.35
1.63
1.52
24
1.20
13
14
1.54
16
1.55
1.40
25
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30
26
1.45
1.32
29
27
1.36
1.35
28
1.86
Br

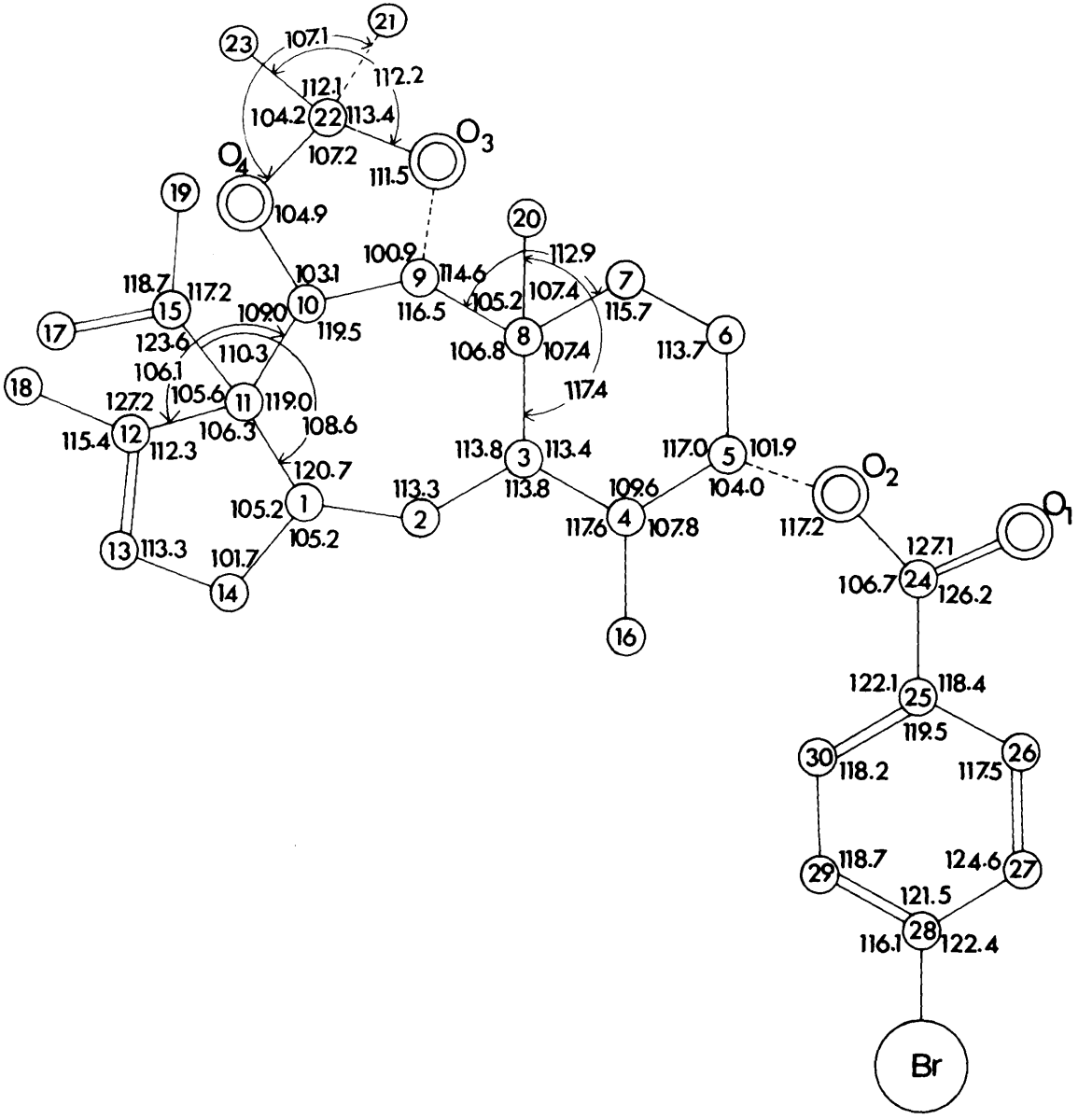

21
23
107.1
112.2
112.1
104.2
22
113.4
O3
O4
107.2
111.5
19
104.9
20
100.9
112.9
103.1
9
114.6
7
118.7
117.2
15
10
116.5
105.2
107.4
115.7
109.0
119.5
17
123.6
110.3
8
106.8
107.4
113.7
6
106.1
18
127.2
105.6
11
119.0
117.4
115.4
12
106.3
108.6
112.3
113.8
3
113.4
117.0
5
101.9
O2
120.7
113.3
113.8
109.6
104.0
O1
105.2
1
2
4
117.6
107.8
117.2
127.1
13
113.3
101.7
105.2
106.7
24
126.2
14
16
122.1
118.4
25
119.5
30
118.2
117.5
26
29
118.7
124.6
27
121.5
28
116.1
122.4
Br

TABLE 2.9

LEAST-SQUARES PLANES

Plane 1 Cyclohexane Ring		Plane 2 Cycloheptane Ring		Plane 3 Cyclopentene Ring		Plane 4 Acetonide Ring	
Atom	Δ(Å)	Atom	Δ(Å)	Atom	Δ(Å)	Atom	Δ(Å)
C(8)	0.265	C(1)	-0.069	C(11)	-0.009	C(9)	0.000
C(3)	-0.271	C(2)	0.063	C(12)	0.018	O(3)	0.000
C(4)	0.211	C(8)	-0.031	C(13)	-0.018	C(22)	0.000
C(5)	-0.141	C(10)	0.018	C(14)	0.009	O(4)*	0.248
C(6)	0.139	C(11)	0.020	C(1)*	0.168	C(10)*	-0.293
C(7)	-0.203	C(3)*	-0.804	C(18)*	-0.481		
C(2)*	-0.111	C(9)*	0.755				
C(9)*	-0.276						
C(16)*	1.687						
C(20)*	1.834	$\overline{\Delta^2}$	= 0.045	$\overline{\Delta^2}$	= 0.014		
O(2)*	-1.673	χ^2	= 92.7	χ^2	= 5.5		

Plane 5 Isopropylidene Group		Plane 6 Phenyl Group		Plane 7 Ester Group	
Atom	Δ(Å)	Atom	Δ(Å)	Atom	Δ(Å)
C(11)	0.013	C(24)	-0.011	C(24)	-0.014
C(15)	-0.041	C(25)	0.015	C(25)	0.004
C(19)	0.013	C(26)	-0.001	O(1)	0.006
C(17)	0.015	C(27)	0.001	O(2)	0.004
		C(28)	-0.014	C(5)*	0.075
		C(29)	-0.024		
		C(30)	0.022		
		Br	0.012		
		O(1)*	-0.134		
		O(2)*	0.191		
		C(5)*	0.294		
$\overline{\Delta^2}$	= 0.024	$\overline{\Delta^2}$	= 0.015	$\overline{\Delta^2}$	= 0.008
χ^2	= 14.9	χ^2(without Br)	= 10.4	χ^2	= 2.6

*These atoms were not used to calculate the least-squares plane.

Plane	Equations for the least-squares planes
1	-0.696 X + 0.099 Y + 0.711 Z = 1.054 Å
2	-0.435 X - 0.743 Y + 0.509 Z = -3.564
3	0.595 X - 0.660 Y + 0.458 Z = 4.610
4	-0.063 X - 0.796 Y + 0.602 Z = -0.608
5	0.395 X + 0.286 Y + 0.873 Z = 9.091
6	0.617 X + 0.387 Y + 0.685 Z = 10.500
7	0.594 X + 0.514 Y + 0.619 Z = 11.327

(X, Y, and Z are coordinates (in Å))

longer one C(16)...C(20) (3.16 Å). In an ideal cyclohexane chair these distances would have been 2.52 Å. (The van der Waals distance between two methyl groups is given by Pauling (1960) as 4.0 Å.) Similar distortions are normal in compounds with 1,3 diaxial methyl groups (Sim, 1967) and the non-bonded distances between them are comparable with the value observed here.

The cycloheptane ring adopts a twisted boat conformation (Friebolin, Mecke, Kabuss, and Lüttringhaus, 1964). The atoms C(3) and C(9) are displaced by -0.80 and +0.76 Å, respectively, from the "best" plane through the atoms C(1), C(2), C(8), C(10), and C(11). This conformation has been found previously in unsaturated seven-membered rings (Friebolin *et al*, 1964). However, it is believed that this is the first time that it has been observed in a saturated seven-membered ring. An examination of a model reveals that this conformation is the only one possible for a cycloheptane ring in this system.

The cyclopentene ring is envelope-shaped and *cis*-fused to the cycloheptane ring. The atoms C(11), C(12), C(13), and C(14) are coplanar and their r.m.s. distance from a least-squares plane is 0.014 Å. The fifth atom, C(1), lies 0.17 Å above this plane. The displacement of the fifth atom in an envelope-shaped five-membered ring

in which all angles are 107.5° was calculated to be 0.23 Å (Sim, 1965). The average of the angles in this cyclopentene ring amounts to 107.8°. In spite of the double bond between C(12) and C(13), C(18) is displaced from the cyclopentene plane by 0.48 Å. This effect must be due to the non-bonded interaction between C(18) and C(17). The plane of the cyclopentene ring makes a dihedral angle of 62° with the cycloheptane plane.

The conformation of the five-membered ring of the acetonide group is half chair since O(4) and C(10) are displaced, respectively, by +0.25 and -0.29 Å from the plane through the atoms C(9), O(3), and C(22). In order to compare this conformation with that of a similar ring system in bis-1:3-dioxa-2-cyclopentyl (Furberg and Hassel, 1950) a plane was calculated through O(3), O(4), and C(22). It was found that C(9) and C(10) lie 0.24 and 0.68 Å, respectively, below this plane. The corresponding atoms in the structure of Furberg and Hassel are displaced by 0.25 and 0.60 Å.

The atoms of the p-bromobenzoate group are not all in one plane. The plane through the aromatic ring, the bromine atom and carbon atom C(24) (all these atoms except bromine are coplanar) is rotated about the C(24)-C(25) bond and makes an angle of 8° with the plane through

the three atoms of the ester group (O(1), C(24), and O(2)) and atom C(25). These four atoms are coplanar and C(5) is displaced by 0.075 Å from their plane. In potassium hydrogen di-p-chlorobenzoate (Mills and Speakman, 1963) the carboxyl group is rotated by 9° from the aromatic plane, a value very close to the one observed here. In o-chlorobenzoic acid (Ferguson and Sim, 1961) the rotation, which was attributed to intramolecular overcrowding, is larger (13.7°). Mathieson (1965) made a survey of the preferred orientation of ester groups. On the basis of a few structures with an ester group in the axial position of a six-membered ring in the chair conformation, he infers that the preferred orientation is that in which the hydrogen atom of the ring carbon atom (here C(5)) is coplanar with the ester group. The preference for this was ascribed to an interaction between this hydrogen atom and the double-bonded oxygen atom (here O(1)) of the ester group. The ester group in this structure is rotated about the C(5)-O(2) bond by 26° from the position predicted by Mathieson. As a result of this rotation the oxygen atom O(1) comes closer to the methyl group (C(16)) of a neighbouring molecule (the non-bonded intermolecular distance O(1)...C(16) (3.28 Å) is shorter than the oxygen-methyl van der Waals distance of 3.4 Å (Pauling, 1960)). This seemingly un-

favourable position of the ester group is in fact preferred to that predicted by Mathieson.

The C_{sp^3}-C_{sp^3} distances range from 1.45 to 1.63 Å with a mean value of 1.54 Å, and the aromatic C-C distances range from 1.32 to 1.46 Å with an average of 1.39 Å. Several of these bond lengths differ from accepted values at a 0.1% significance level. Since there are no obvious explanations for these deviations it is likely that the calculated e.s.d.'s are underestimated. The main reasons for this are probably the block-diagonal approximation in the least-squares calculations and the limited amount of data. A doubling of the e.s.d.'s may therefore be reasonable and is assumed in the following discussion.

The C(24)-C(25) bond length (1.552 Å) agrees with the value found in o-chlorobenzoic acid (1.521 ± 0.009 Å) (Ferguson and Sim, 1961) but is on the long side of the value in benzoic acid (1.48 ± 0.016 Å) (Sim, Robertson, and Goodwin, 1955), even though not significantly so. Since bromine withdraws electrons from the aromatic ring the C(24)-C(25) is expected to have less double-bond character than the corresponding bond in benzoic acid. The C-O single bond, O(2)-C(5), is much longer (1.533 Å) than the average of the four C-O bonds in the acetonide ring (1.411 Å). However, as will be shown in Chapter IV, it is

in agreement with values found in various other esters. All other bond lengths are normal.

As previously mentioned, the cyclohexane ring is somewhat flattened and two of its angles are significantly larger than the tetrahedral value. From a survey of several steroid structures Geise, Altona, and Romers (1967) observed that the valency angles at secondary and tertiary carbon atoms are larger than tetrahedral. These observations are in agreement with theoretical calculations (Bucourt and Heinaut, 1965) which gave the values of 111.1° in unsubstituted cyclohexane in the chair conformation and 109.5 - 111.0° in substituted cyclohexanes. Geise *et al* (1967) also observed that valency angles at quaternary carbon atoms are smaller than tetrahedral. In view of this, only the angle C(4)-C(5)-C(6) (117.0°) deviates significantly. This angle and the somewhat large angle C(6)-C(7)-C(8) (115.7°) are adjacent to the atoms C(4) and C(8) to which the two methyl carbon atoms (C(16) and C(20)) are bonded. These deviations are therefore associated with the previously mentioned bending of the two diaxial methyl groups away from each other. Due to the same bending the angles C(3)-C(4)-C(16) (117.6°) and C(3)-C(8)-C(20) (117.4°) have increased values. Both the exocyclic angles around C(5) are significantly smaller than the normal value.

The angles in the seven-membered ring at the junctions with the two adjacent five-membered rings are significantly larger than tetrahedral. In order to form a *cis*-junction with the cyclopentene ring a rotation about the C(1)-C(11) bond has to take place and hence the angles at these two atoms are enlarged. The *trans*-junction with the acetonide ring causes less strain and this is manifested by the smaller increase in the C(8)-C(9)-C(10) angle. A repulsion between hydrogen atoms H(3) and H(10) may also contribute to the flattening of the cycloheptane ring.

In the five-membered rings the mean value of the valency angles at the single-bonded atoms is 105.1°. The usual mean value in saturated five-membered rings is 105° (Sim, 1965). As expected, the two valency angles at the double-bonded atoms C(12) and C(13) in the cyclopentene ring are both smaller than 120°. The angle C(11)-C(12)-C(18) (127.2°) is significantly larger than 120°. This is due to the previously mentioned repulsion between C(18) and C(17).

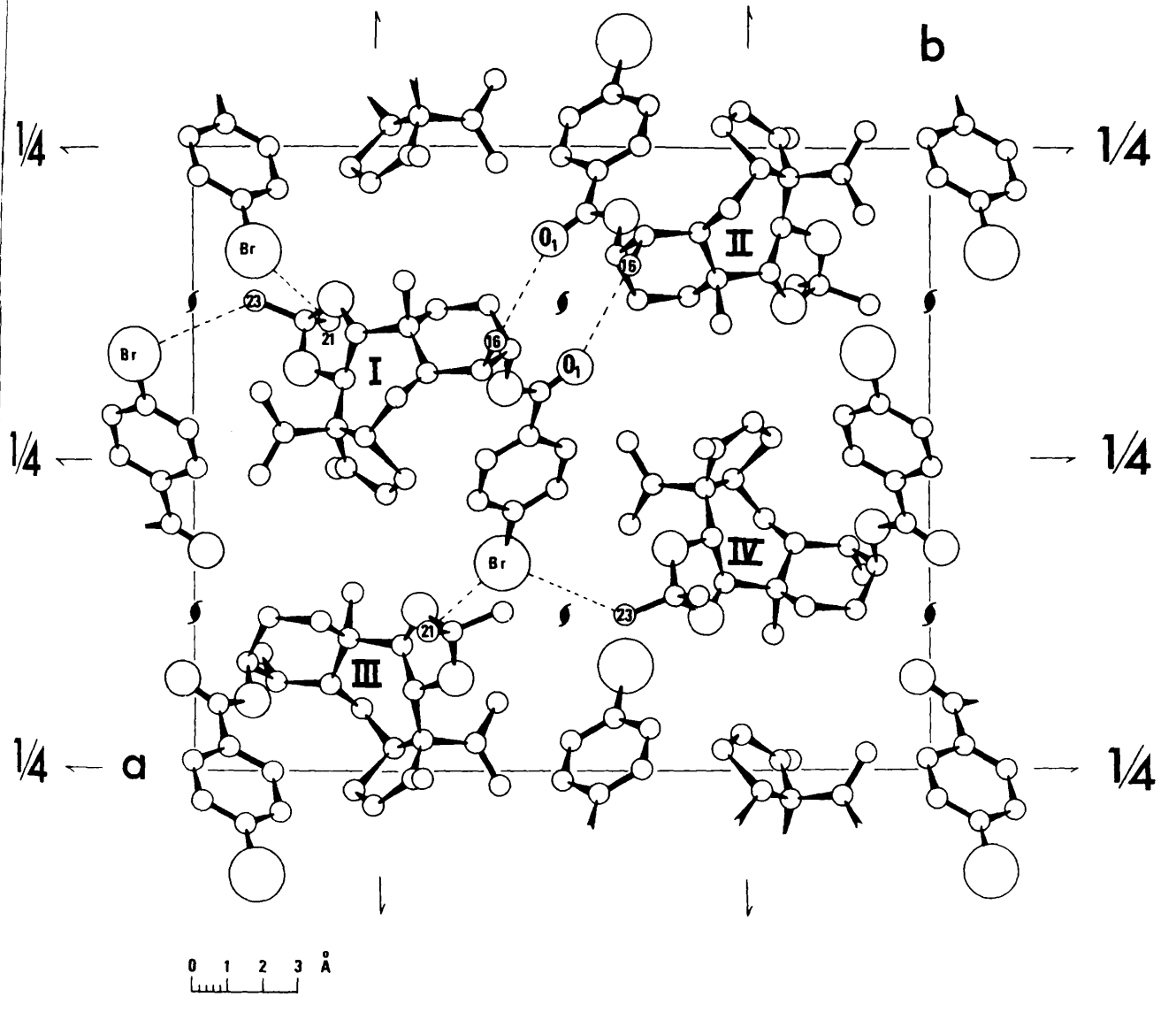
The bond angles at C(24) agree well with the corresponding angles in un-ionised carboxyl groups (Hahn, 1957); the angle C(25)-C(24)-O(2) is approximately tetrahedral and the two angles C(25)-C(24)-O(1) and O(2)-C(24)-O(1) are close to 125°.

8. Molecular packing

The molecular arrangement viewed along the c-axis is shown in Figure 2.4. Of the intermolecular contacts less than 4.0 Å (Table 2.8) the following are shorter than the van der Waals distances given by Pauling (1960) (3.40 Å for O...C_{methyl} and 3.95 Å for Br...C_{methyl}): C(16)...O(1) (3.28 Å), Br...C(21) (3.60 Å), and Br...C(23) (3.76 Å). Since none of these contacts can be hydrogen bonds it is unlikely that the discrepancies are meaningful. The short distances are marked with broken lines on the packing diagram. The two broken lines from atoms O(1) and C(16) in equivalent position I go to the atoms C(16) and O(1) of two different molecules in equivalent position II, the former in cell (0,0,-1) and the latter in cell (0,0,0).

Figure 2.4

A packing diagram viewed along the c-axis.

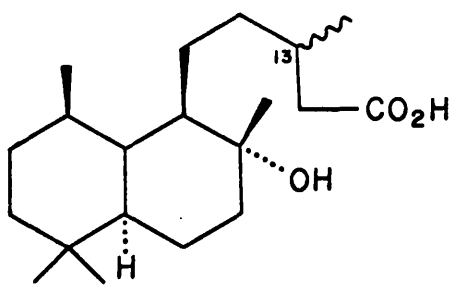

b
1/4
1/4
1/4
1/4
1/4
a
Br
Br
Br
23
21
16
O_1
I
II
III
IV
0 1 2 3 Å

CHAPTER III

Crystal Structure Analysis of p-Bromophenacyl Labdanolate

I. Introduction

Gum labdanum is used as a fixative in perfumery and is obtained from *Cistus ladaniferus* L. ("rock-rose") by boiling the wood of the bramble in water. Labdanolic acid, $C_{20}H_{36}O_3$, was first isolated by Cocker and Halsall (1956a) from Spanish gum labdanum. The structure (I) of this new bicyclic diterpene hydroxy-acid was described in a subsequent publication (Cocker and Halsall, 1956b), but the configuration at C(13) remained undetermined.



I

Bory and Lederer (1957) assigned the (R)-configuration (notation of Cahn, Ingold, and Prelog, 1956) to C(13) in labdanolic acid. This assignment was based on the assumption that in a diastereomeric pair of β-methyl carboxylic

acids, the more laevorotatory stereoisomer has the (R)-configuration at the β-carbon atom. This was re-investigated by Bigley, Rogers, and Barltrop (1960) in view of these authors' discovery that an assignment of the configuration based on molecular rotations may be erroneous if hydrogen bonding occurs. However, they interpreted the infrared spectra of methyl labdanolate and methyl 13-epilabdanolate as showing no evidence of intramolecular hydrogen bonding, and they therefore assumed that Bory and Lederer's (1957) assignment had been correct. From infrared studies of several compounds of the labdane type (Baker, Eglinton, Gonzales, Hamilton, and Raphael, 1962) it was shown that intramolecular hydrogen bonding does in fact occur. Graham and Overton (1964) showed that eperuic and labdanolic acids possess the same configuration at C(13), being otherwise antipodal. On the basis of chemical degradation Overton and Renfrew (1967) concluded that the configuration at C(13) in these acids is (S) but by mistake called it (R). This X-ray analysis was undertaken in order to establish unambiguously the stereochemistry at C(13) in labdanolic acid as well as to confirm the rest of the molecular configuration.

2. Crystal data

p-Bromophenacyl labdanolate, $C_{28}H_{41}O_4Br$, F.W. = 521.4, m.p. 124-125°C. Monoclinic, a = 11.55 ± 0.01, b = 6.05 ± 0.01 c = 19.90 ± 0.02 Å; β = 99.0 ± 0.2°. V = 1373 Å^3. D_m = 1.28 g.cm.$^{-3}$ (by flotation in aqueous potassium iodide), Z = 2, D_x = 1.26 g.cm.$^{-3}$. F(000) = 552. Space group $P2_1$ (No. 4). Linear absorption coefficient μ = 24.9 cm.$^{-1}$ for Cu Kα radiation (λ = 1.5418 Å).

3. Crystallographic measurements

p-Bromophenacyl labdanolate crystallises as colourless, long well-formed needles with the unique b-axis parallel to the needle axis. The crystals are stable in the air.

Oscillation, Weissenberg, and precession photographs were taken with a crystal mounted along the needle axis using Cu Kα radiation. The unit-cell parameters were obtained from oscillation, zero-layer Weissenberg and precession photographs by taking weighted averages. The standard deviations given for the cell dimensions are the root-mean-square deviations obtained from the individual measurements. The space group ($P2_1$) was determined from the systematic absences (0k0 absent if k is odd) and from the knowledge that the molecule is optically active ($[\alpha]_D$ = -10°). Non-integrated three-dimensional intensity

data were collected with an equi-inclination Weissenberg camera using the multiple-film technique. Layers h0ℓ through h5ℓ were obtained. The crystals deteriorate after 7-9 days of exposure in the X-ray beam. This problem was overcome by using a long needle (0.13 × 0.13 × 3.50 mm.) with only part of it exposed at a time. The crystal was moved in a direction perpendicular to the X-ray beam as it deteriorated. All the intensity data were therefore collected from different parts of the same crystal specimen.

The photographs were indexed with respect to a right-handed set of axes (Peerdeman and Bijvoet, 1956). Of the 3137 reflexions accessible within the Cu sphere 1672 (53%) were measured visually with a calibrated intensity strip. Reflexions which were too weak to be measured were not included in any of the calculations. The data were corrected for Lorentz and polarisation factors. No absorption correction was considered necessary since μR has the low value of 0.16. In the initial stages of the structure determination the data were put on an approximate absolute scale by making $k \sum_{hk\ell} |F_o| = \sum_{hk\ell} |F_c|$ for each layer. The layer-scale factors were later refined by least-squares methods.

4. Structure determination

The structure was solved by the heavy-atom method

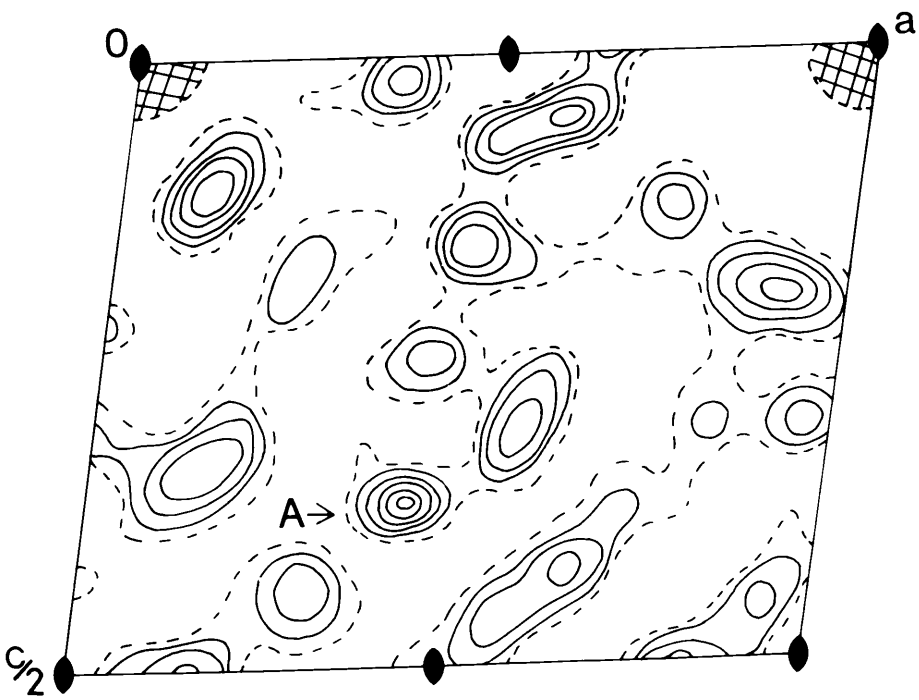
($\Sigma f_H^2/\Sigma f_L^2$ = 0.94 at sinθ = 0), first in the h0ℓ projection and then in three dimensions.

(a) Analysis in the h0ℓ projection

The plane group of this projection is p2 with the two equivalent positions (x,z) and ($\bar{x}$,$\bar{z}$). The Patterson map, whose symmetry is also p2, will thus contain a vector peak at (2x,2z) with single weight. A Patterson synthesis computed with unsharpened data contained five peaks with about equal heights and it was not clear which of these represented the Br-Br vector. Another Patterson synthesis was then computed, using data sharpened to point atom with respect to bromine. This map is shown in Figure 3.1. The lowest of the five peaks became the highest one and it is marked "A" in the map. It was interpreted as being the Br-Br vector peak and gave the coordinates for bromine as x = 0.218, z = 0.184 (by Booth's (1948b) interpolation method). A structure-factor calculation with Br in this position gave an R-factor of 60%. An electron-density projection calculated with the observed amplitudes and Br phase angles revealed the entire structure. When all the atoms were included in a structure-factor calculation R reduced to 41%. The x and z coordinates for all the atoms were then refined with a minimum-residual programme

Figure 3.1

Sharpened Patterson map in the h0ℓ projection.
Contours are drawn at arbitrary intervals.


0
a
A→
c/2

(Bhuiya and Stanley, 1963) and in five cycles R was lowered to 23%.

(b) Three-dimensional analysis

In space group $P2_1$ the origin in the y-direction is not fixed. This coordinate of the bromine atom was put at $y = \frac{1}{4}$ and a structure-factor calculation with this atom only gave an R-factor of 49%. The subsequent three-dimensional electron-density map contained pseudo-mirror planes parallel to (010) at $y = \frac{1}{4}$, 3/4, etc. Since the b-axis is short, the pseudo-mirror planes are close to each other, and only a few peaks were resolved from their mirror images. It was therefore difficult to determine the y-coordinates of the atoms even though the structure had been solved in projection. Two carbon atoms (C(6) and C(7)) from the decalin system which deviated most from $y = \frac{1}{4}$ were selected first. The rest of the atoms were resolved gradually in six further rounds of structure-factors and electron-density calculations. At this stage R was 27%. Throughout the structure determination an overall $U_{iso} = 0.05$ Å^2 was assumed.

5. Structure refinement

Positional and thermal-vibration parameters as well as layer-scale factors were refined using the block-

diagonal approximation of the least-squares method. The y coordinate of the bromine atom was held constant at ¼ throughout the refinement. The function minimised was $M = \sum_{hk\ell} w(|F_o| - |F_c|)^2$.

Six cycles of isotropic refinement lowered R to 20.4%. The data were then put on a common absolute scale using the refined layer-scale factors. During the following anisotropic refinement only one overall scale factor was refined. In the polar space group $P2_1$ an error in the y coordinate of the bromine would be introduced unless corrections for anomalous dispersion are applied (Ueki *et al*, 1966; Cruickshank and McDonald, 1967). The absolute configuration of labdanolic acid was known (from a synthesis starting out with sclareol of established configuration (Bory and Lederer, 1957)) and it is the one used here. Corrections for anomalous dispersion by bromine were applied during the anisotropic refinement. Convergence was reached after eight cycles and the final R was 11.4%. Throughout the refinement a shift factor of 0.8 was used. After the last cycle no shifts were larger than 0.1σ in the coordinates and 0.2σ in the thermal parameters.

A summary of the least-squares refinement is outlined

below ($R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = \Sigma w\Delta^2/\Sigma wF_o^2$) :

Cycle No.	R	R'	Parameters refined
1	0.272		
2	0.227		x,y,z, U_{iso} for Br,
3	0.213		O, C + layer-scale
4	0.205		factors
5	0.204		
6	0.204		
7	0.204	0.0920	
8	0.151	0.0513	
9	0.135	0.0320	x,y,z, U_{ij} (i,j = 1,2,3)
10	0.125	0.0283	for Br, O, C
11*	0.123	0.0286	+ one overall scale
12	0.116	0.0249	factor
13	0.115	0.0243	
14	0.115	0.0242	
15	0.114	0.0241	(structure factors only)

* Adjustments in the parameters of the weighting scheme were made.

During the isotropic refinement the terms were assigned unit weights, but during the anisotropic refinement the following weighting scheme was used: $w = (p_1 + |F_o| +$

$p_2|F_o|^2 + p_3|F_o|^3)^{-1}$. The p-parameters were adjusted during the refinement in order to minimise the variation of $w\Delta^2$ as a function of $|F_o|$. At the end of the refinement the final values ($p_1 = 4.0$, $p_2 = 0.05$, $p_3 = 0.0005$) gave the following analysis of averaged $w\Delta^2$ as a function of $|F_o|$ and of $\sin\theta/\lambda$:

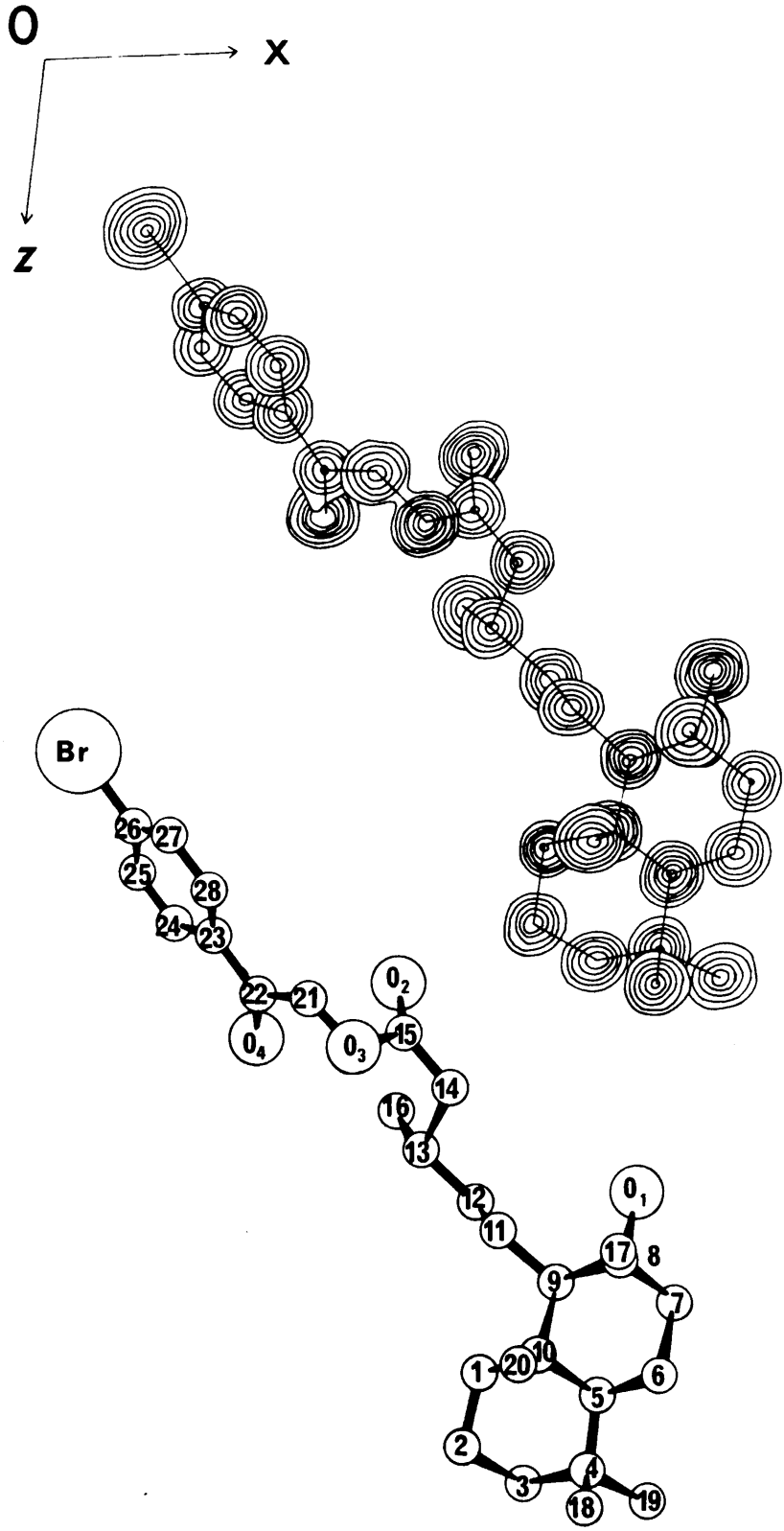
$\lvert F_o \rvert$	$\langle w\Delta^2 \rangle$	No. of reflexions	$\sin\theta/\lambda$	$\langle w\Delta^2 \rangle$	No. of reflexions
0- 7	0.075	592	0.0-0.2	0.341	114
7- 15	0.128	570	0.2-0.4	0.135	666
15- 29	0.188	347	0.4-0.6	0.089	831
29- 59	0.181	139	0.6-0.8	0.129	61
59-117	0.119	24			

There is greater variation in $\langle w\Delta^2 \rangle$ as a function of $\sin\theta/\lambda$ than of $|F_o|$, presumably because the hydrogen atoms were not included. It would therefore have been better to use a weighting scheme which is also a function of $\sin\theta/\lambda$.

At the end of the refinement a difference Fourier synthesis was calculated. Some diffuse maxima occurred in positions stereochemically acceptable for hydrogen atoms but it was not possible to determine their coordinates. The composite final three-dimensional Fourier map and its interpretation can be seen in Figure 3.2. The numbering scheme is also shown in this diagram.

Figure 3.2

Composite three-dimensional electron-density map, viewed along the b-axis, and its interpretation with the numbering scheme. The contours start at 1 $e\mathring{A}^{-3}$ and are drawn at intervals of 1 $e\mathring{A}^{-3}$ except around bromine where the intervals are 5 $e\mathring{A}^{-3}$.


O
X
Z
Br
26
27
25
28
24
23
22
21
O_2
O_4
O_3
15
14
16
13
12
11
O_1
17
8
9
7
1
20
10
6
5
2
4
3
18
19

Atomic scattering factors and the real and imaginary parts of anomalous-dispersion corrections for bromine were taken from International Tables for X-Ray Crystallography (1962).

The final coordinates and the thermal parameters are listed in Tables 3.1 and 3.2. The e.s.d.'s were derived from the inverse of the least-squares matrix. Table 3.3 shows the observed and calculated structure factors. Orthogonal coordinates (in Å) are given in Table 3.4 and principal values of vibration tensors in Table 3.5. Molecular dimensions with e.s.d.'s and non-bonded distances can be seen in Tables 3.6 and 3.7, respectively.

TABLE 3.1

FRACTIONAL COORDINATES AND E.S.D.s

ATOM	x/a	y/b	z/c
Br(1)	0.2116 ± 2	0.2500 ± 0	0.1843 ± 1
O(1)	1.2969 ± 11	0.3726 ± 21	0.6726 ± 5
O(2)	0.8295 ± 9	0.2174 ± 22	0.4405 ± 5
O(3)	0.7617 ± 9	0.4743 ± 18	0.5055 ± 5
O(4)	0.5859 ± 11	0.1923 ± 24	0.4924 ± 7
C(1)	1.0488 ± 10	0.2467 ± 27	0.8517 ± 6
C(2)	1.0354 ± 13	0.2394 ± 31	0.9288 ± 7
C(3)	1.1531 ± 16	0.1681 ± 25	0.9715 ± 7
C(4)	1.2616 ± 12	0.2959 ± 22	0.9612 ± 6
C(5)	1.2660 ± 11	0.3136 ± 18	0.8823 ± 6
C(6)	1.3734 ± 11	0.4362 ± 27	0.8664 ± 7
C(7)	1.3861 ± 13	0.3894 ± 29	0.7886 ± 7
C(8)	1.2807 ± 12	0.4624 ± 21	0.7400 ± 7
C(9)	1.1698 ± 12	0.3495 ± 21	0.7604 ± 6
C(10)	1.1511 ± 11	0.3936 ± 20	0.8368 ± 6
C(11)	1.0569 ± 13	0.3860 ± 25	0.7045 ± 7
C(12)	1.0101 ± 13	0.1687 ± 23	0.6742 ± 7
C(13)	0.9022 ± 12	0.1876 ± 26	0.6159 ± 7
C(14)	0.9411 ± 12	0.3083 ± 27	0.5516 ± 7
C(15)	0.8443 ± 13	0.3170 ± 30	0.4929 ± 7

C(16)	0.8517 ± 16	-0.0374 ± 28	0.5959 ± 8
C(17)	1.2761 ± 15	0.7104 ± 33	0.7333 ± 8
C(18)	1.2651 ± 16	0.5182 ± 27	0.9986 ± 8
C(19)	1.3737 ± 16	0.1694 ± 26	0.9967 ± 8
C(20)	1.1205 ± 14	0.6376 ± 22	0.8460 ± 7
C(21)	0.6679 ± 14	0.5113 ± 30	0.4514 ± 7
C(22)	0.5798 ± 12	0.3318 ± 26	0.4460 ± 7
C(23)	0.4892 ± 11	0.3157 ± 27	0.3831 ± 7
C(24)	0.4193 ± 15	0.1213 ± 33	0.3688 ± 8
C(25)	0.3393 ± 16	0.1043 ± 30	0.3128 ± 8
C(26)	0.3235 ± 11	0.2879 ± 37	0.2649 ± 6
C(27)	0.3891 ± 13	0.4663 ± 36	0.2769 ± 8
C(28)	0.4699 ± 13	0.4891 ± 31	0.3347 ± 8

TABLE 3.2

ANISOTROPIC TEMPERATURE PARAMETERS AND E.S.D.s (A^{o2})

ATOM	U 11	U 22	U 33	2U 23	2U 31	2U 12
Br(1)	0.1071 15	0.1667 28	0.0871 12	0.0213 34	-0.0555 22	-0.0988 37
O(1)	0.1101 91	0.0601 78	0.0597 59	0.0002 107	0.0397 122	-0.0015 134
O(2)	0.0790 66	0.0662 77	0.0614 53	-0.0344 113	-0.0227 94	0.0353 124
O(3)	0.0773 68	0.0415 66	0.0628 56	-0.0321 97	-0.0094 97	0.0146 105
O(4)	0.0887 78	0.0704 90	0.1040 85	0.0623 148	-0.0191 133	-0.0269 139
C(1)	0.0423 63	0.0472 91	0.0617 69	-0.0285 148	0.0103 105	-0.0060 132
C(2)	0.0681 83	0.0504 93	0.0653 77	-0.0069 157	0.0200 128	-0.0242 155
C(3)	0.0995 116	0.0344 94	0.0572 78	0.0031 130	0.0292 157	-0.0053 161
C(4)	0.0745 81	0.0136 73	0.0611 71	0.0020 122	-0.0224 120	-0.0078 128
C(5)	0.0567 68	0.0040 66	0.0549 62	-0.0072 98	0.0029 105	0.0026 105
C(6)	0.0428 71	0.0559 103	0.0641 82	-0.0030 142	-0.0177 122	-0.0035 129
C(7)	0.0532 80	0.0628 106	0.0613 81	0.0040 146	0.0210 133	-0.0251 146
C(8)	0.0593 78	0.0122 75	0.0694 80	-0.0002 117	0.0287 127	0.0036 117

C(9)	0.0592 75	0.0190 76	0.0550 69	0.0053 109	-0.0142 114	0.0072 113
C(10)	0.0468 66	0.0159 68	0.0507 64	-0.0013 104	-0.0097 104	0.0031 101
C(11)	0.0633 84	0.0332 81	0.0576 73	0.0007 123	-0.0062 129	0.0114 128
C(12)	0.0728 87	0.0291 84	0.0542 70	0.0020 116	-0.0024 127	-0.0060 133
C(13)	0.0591 78	0.0453 97	0.0551 70	-0.0118 129	-0.0155 119	-0.0158 134
C(14)	0.0563 76	0.0485 95	0.0585 72	-0.0024 133	0.0035 117	-0.0076 141
C(15)	0.0656 85	0.0614 106	0.0551 73	0.0046 143	0.0142 129	-0.0053 159
C(16)	0.0981 117	0.0403 103	0.0710 90	-0.0022 151	-0.0091 166	-0.0749 183
C(17)	0.0891 110	0.0573 117	0.0724 92	-0.0119 170	0.0478 165	-0.0407 189
C(18)	0.1027 124	0.0238 85	0.0653 84	-0.0251 132	-0.0099 161	-0.0170 161
C(19)	0.1071 128	0.0318 100	0.0703 93	0.0308 145	-0.0119 173	0.0300 171
C(20)	0.0887 100	0.0119 73	0.0561 72	-0.0140 110	-0.0006 137	0.0149 135
C(21)	0.0677 92	0.0568 103	0.0587 78	-0.0071 149	-0.0088 134	-0.0041 160
C(22)	0.0496 70	0.0479 95	0.0646 78	0.0179 137	0.0002 120	0.0125 130
C(23)	0.0503 71	0.0510 99	0.0597 73	0.0059 134	0.0223 115	0.0251 137
C(24)	0.0727 104	0.0729 122	0.0674 92	-0.0015 175	0.0246 159	-0.0069 179

C(25)	0.0691 95	0.0586 104	0.0705 90	-0.0261 163	0.0287 148	-0.0093 164
C(26)	0.0455 68	0.1169 156	0.0431 60	-0.0244 177	-0.0519 106	-0.0033 181
C(27)	0.0495 81	0.0869 138	0.0730 92	0.0317 184	-0.0254 136	-0.0258 166
C(28)	0.0609 89	0.0579 105	0.0727 92	0.0178 158	0.0127 147	-0.0073 164

TABLE 3.3

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	|Fo|	|Fc|
0	0	2	23.7	24.7
0	0	3	38.6	47.5
0	0	4	39.4	35.1
0	0	5	22.5	20.1
0	0	6	82.9	77.3
0	0	7	21.6	19.7
0	0	8	13.3	14.7
0	0	9	22.4	24.4
0	0	10	6.5	7.9
0	0	11	20.8	20.3
0	0	12	12.6	15.5
0	0	13	14.5	13.5
0	0	14	12.1	12.5
0	0	16	19.2	23.0
0	0	17	10.1	12.5
0	0	18	9.3	10.4
0	0	19	9.5	9.0
0	0	22	6.6	4.9
0	1	0	17.8	10.9
0	1	2	89.6	83.0
0	1	3	8.4	14.7
0	1	4	11.5	6.4
0	1	5	41.8	34.2
0	1	6	6.3	5.1
0	1	7	11.6	10.5
0	1	8	39.8	30.8
0	1	9	13.6	4.4
0	1	10	3.8	2.5
0	1	11	19.7	21.6
0	1	12	44.3	62.0
0	1	13	45.2	48.1
0	1	14	43.9	38.6
0	1	15	32.3	34.6
0	1	16	47.9	45.0
0	1	17	7.0	6.2
0	1	18	8.9	8.0
0	1	19	6.7	5.2
0	1	20	7.4	5.6
0	1	21	7.0	6.2
0	1	23	8.9	8.0
0	1	24	6.7	5.2
0	2	1	42.0	39.1
0	2	2	28.2	22.1
0	2	3	23.6	34.0
0	2	4	3.8	3.8
0	2	5	31.6	29.2
0	2	6	50.8	48.4
0	2	7	11.8	15.3
0	2	8	24.6	33.3
0	2	9	26.6	32.0
0	2	10	14.3	14.5
0	2	11	39.1	37.3
0	2	12	23.5	24.0
0	2	13	26.7	28.4
0	2	14	28.5	31.9
0	2	15	13.1	14.1
0	2	16	19.5	20.7
0	2	17	8.6	8.8
0	2	18	8.6	6.7
0	2	19	9.0	5.0
0	2	22	8.1	6.1
0	2	23	7.2	4.6
0	3	1	39.2	29.7
0	3	2	68.1	60.3
0	3	3	41.5	46.1
0	3	4	42.1	43.0
0	3	5	80.1	82.6
0	3	6	17.7	15.0
0	3	7	79.1	70.3
0	3	10	22.6	29.6
0	3	13	16.3	17.0
0	3	15	15.6	17.3
0	3	16	11.9	11.8
0	3	18	8.4	7.8
0	3	19	7.4	8.6
0	3	23	5.7	4.8
0	4	0	63.9	64.8
0	4	1	7.3	8.7
0	4	2	54.7	43.4
0	4	3	43.3	39.7
0	4	4	12.3	10.8
0	4	5	31.1	29.3
0	4	6	7.8	9.6
0	4	7	14.2	14.7
0	4	8	19.3	19.2
0	4	9	8.9	6.7
0	4	10	26.0	27.8
0	4	16	9.3	7.6
0	4	17	10.1	10.5
0	4	18	7.5	7.9
0	4	20	6.5	6.6
0	4	22	6.4	6.8
0	5	1	5.9	4.2
0	5	2	9.7	11.0
0	5	3	69.9	61.5
0	5	4	67.7	56.0
0	5	5	29.4	31.4
0	5	6	15.0	15.4
0	5	7	38.6	36.6
0	5	8	17.1	15.8
0	5	9	8.0	9.8
0	5	10	18.8	19.6
0	5	11	17.9	18.3
0	5	13	15.9	17.1
0	5	14	7.7	7.7
0	5	16	15.3	14.1
0	5	19	14.8	12.2
0	6	0	33.6	26.6
0	6	2	35.6	30.5
0	6	3	39.5	28.0
0	6	5	23.5	20.5
0	6	6	13.5	15.3
0	6	7	20.9	22.5
0	6	8	14.4	16.2
0	6	9	25.0	21.0
0	6	12	14.1	15.2
0	6	15	18.2	15.8
0	7	1	13.0	12.4
0	7	2	9.6	9.0
0	7	3	25.7	24.3
0	7	4	12.0	13.1
0	7	6	16.6	16.5
0	7	8	16.9	16.1
0	7	9	14.9	16.9
0	7	11	19.2	18.6
0	7	14	10.7	13.5
0	7	16	13.6	10.8
0	7	19	9.4	8.6
0	8	2	51.3	44.4
0	8	3	17.3	16.1
0	8	4	15.3	14.6
0	8	6	9.9	10.8
0	8	7	17.5	16.1
0	8	8	14.6	16.3
0	8	12	7.7	6.6
0	8	13	8.7	10.4
0	9	0	11.5	11.2
0	0	4	8.5	9.0
0	0	6	14.9	16.0
0	0	11	7.4	9.8
0	0	12	8.4	8.4
0	0	14	10.9	10.1
0	1	1	12.1	12.3
0	1	2	19.7	18.0
0	1	3	7.8	8.0
0	1	13	5.8	6.3
0	1	15	8.4	6.2
0	1	16	7.6	9.1
0	1	17	6.1	6.7
0	1	18	15.1	28.0
0	1	22	16.1	7.1
0	1	23	67.7	70.0
0	1	24	69.6	80.7
0	2	0	35.3	37.0
0	2	2	50.2	51.8
0	2	3	26.0	23.9
0	2	4	31.0	25.7
0	2	5	59.0	66.8
0	2	6	65.4	52.1
0	2	7	14.4	12.4
0	2	8	21.6	23.2
0	2	9	16.9	18.8
0	2	10	12.8	15.9
0	2	11	17.2	18.2
0	2	12	9.8	8.0
0	2	13	12.7	11.9
0	2	14	7.8	6.9
0	2	15	53.9	46.8
0	2	16	20.9	28.9
0	2	17	13.9	14.4
0	2	18	7.4	8.3
0	2	19	7.5	6.2
0	2	20	5.4	5.4
0	2	21	4.3	3.8
0	2	22	38.4	30.7
0	2	23	44.1	43.0
0	2	24	7.6	10.3
0	3	0	54.3	51.3
0	3	2	17.5	24.5
0	3	3	12.1	13.2
0	3	4	52.1	49.9
0	3	5	28.8	33.2
0	3	6	5.2	4.8
0	3	7	27.6	34.5
0	3	8	9.2	11.7
0	3	9	12.5	13.3
0	3	10	25.8	26.7
0	3	11	8.5	10.1
0	3	12	8.4	10.5
0	3	13	5.2	5.9
0	3	14	4.4	3.8
0	3	15	11.5	13.2
0	3	16	8.4	8.4
0	3	17	4.4	3.4
0	3	18	8.6	7.2
0	3	19	50.5	46.7
0	3	20	10.4	15.3
0	3	21	43.3	37.6
0	3	22	45.6	41.8
0	3	23	7.0	5.7
0	3	24	21.4	28.9
0	4	0	24.6	25.7
0	4	1	27.6	31.6
0	4	2	28.1	34.3
0	4	3	20.6	24.8
0	4	4	8.3	9.5
0	4	5	17.2	17.7
0	4	6	23.3	27.0
0	4	7	13.4	13.4
0	4	8	12.1	13.7
0	4	9	7.5	8.4
0	4	10	5.6	5.7
0	4	11	8.8	8.0
0	4	12	4.4	4.3
0	4	13	17.3	15.5
0	4	14	48.4	46.9
0	4	15	19.4	14.6
0	4	16	24.0	20.0
0	4	17	75.2	73.5
0	4	18	20.3	17.0
0	4	19	8.2	6.0
0	4	20	16.5	21.7
0	4	21	5.6	5.4
0	4	22	27.2	28.4
0	4	23	14.4	15.5
0	4	24	14.0	15.6
0	5	0	13.3	11.7
0	5	1	15.0	18.0
0	5	2	6.3	6.2
0	5	3	16	5.7
0	5	4	18	10.2
0	5	5	19	4.3
0	5	6	21	7.0
0	5	7	22	3.1
0	5	8	1	37.0
0	5	9	2	10.5
0	5	10	3	15.4
0	5	11	4	63.0
0	5	12	5	9.5
0	5	13	6	16.8
0	5	14	7	22.7
0	5	15	8	10.2
0	5	16	9	21.6
0	5	17	10	9.2
0	5	18	11	6.5
0	5	19	12	15.5
0	5	20	14	6.3
0	5	21	15	11.5
0	5	22	16	6.5
0	5	23	17	3.5
0	5	24	18	24.8
0	6	0	19	14.9
0	6	1	20	8.5
0	6	2	21	8.6
0	6	3	22	7.8
0	6	4	23	11.6
0	6	5	24	8.8
0	6	6	1	12.5
0	6	7	2	11.5
0	6	8	3	13.7
0	6	9	4	13.8
0	6	10	5	13.1
0	6	11	6	20.8
0	6	12	8	8.4
0	6	13	9	10.7
0	6	14	10	10.7
0	6	16	11	4.8
0	6	18	12	8.8
0	6	19	13	6.0
0	7	1	14	23.2
0	7	2	15	31.7
0	7	3	16	11.1
0	7	4	17	18.4
0	7	5	18	21.0
0	7	6	19	19.0
0	1	9	31.5	29.2
0	1	10	41.4	48.2
0	1	11	4.4	3.1
0	1	12	35.3	34.6
0	1	13	5.9	7.1
0	1	14	9.6	10.1
0	1	16	10.9	12.2
0	1	17	11.5	11.4
0	1	18	5.2	5.2
0	1	20	5.0	4.2
0	1	23	10.7	7.6
0	1	24	4.3	2.9
0	2	0	12.4	14.0
0	2	2	10.5	9.6
0	2	3	56.1	56.9
0	2	4	53.1	56.4
0	2	5	38.9	36.2
0	2	6	36.6	36.6
0	2	7	33.5	34.7
0	2	8	47.9	46.6
0	2	9	12.3	13.5
0	2	10	12.8	13.0
0	2	11	21.4	19.7
0	2	12	13.7	13.3
0	2	13	11.0	12.6
0	2	14	32.4	34.7
0	2	15	10.6	11.8
0	2	16	13.2	11.3
0	2	18	5.2	4.8
0	2	19	7.5	6.2
0	2	20	5.4	5.4
0	2	22	4.3	3.8
0	2	24	27.6	34.5
0	3	1	7.7	9.2
0	3	2	11.7	11.8
0	3	3	7.8	7.7
0	3	4	5.2	6.2
0	3	5	7.9	8.4
0	3	6	4.4	5.2
0	3	7	12.8	13.0
0	3	8	4.2	4.1
0	3	9	5.9	5.8
0	3	10	4.9	4.9
0	3	11	7.9	7.1
0	3	12	7.9	8.5
0	3	13	9.3	7.9
0	3	15	5.9	5.0
0	3	16	4.0	3.1
0	4	1	9.9	9.6
0	4	2	6.9	6.4
0	4	3	7.9	6.8
0	4	4	4.4	5.2
0	4	5	12.2	14.4
0	4	6	16.6	17.5
0	4	7	28.3	26.7
0	4	8	12.2	14.4
0	4	9	13.0	14.3
0	4	10	6.0	6.8
0	4	11	5.3	5.0
0	4	12	14.7	13.5
0	4	13	5.3	5.6
0	4	14	5.2	5.4
0	4	15	5.0	4.4
0	4	16	4.0	3.1
0	5	1	9.9	9.6
0	5	2	6.9	6.4
0	5	3	5.2	4.8
0	5	4	13.0	13.4
0	5	5	5.9	5.4
0	5	6	5.3	4.9
0	5	7	6.4	6.4
0	5	8	5.3	4.8
0	5	9	5.2	4.9
0	5	10	5.7	4.8
0	5	11	6.4	5.9
0	5	12	4.2	3.8
0	5	13	5.2	4.9
0	5	14	5.1	4.8
0	5	15	4.4	3.4
0	5	16	4.2	3.4
0	6	1	6.9	6.2
0	6	2	5.4	5.4
0	6	3	4.2	3.8
0	6	4	4.3	3.4
0	6	5	4.2	3.4
0	6	6	4.2	3.4
0	6	7	4.2	3.4
0	6	8	4.2	3.4
0	6	9	4.2	3.4
0	6	10	4.2	3.4
0	6	11	4.2	3.4
0	6	12	4.2	3.4
0	6	13	4.2	3.4
0	6	14	4.2	3.4
0	6	15	4.2	3.4
0	6	16	4.2	3.4
0	7	1	4.2	3.4
0	7	2	4.2	3.4
0	7	3	4.2	3.4
0	7	4	4.2	3.4
0	7	5	4.2	3.4
0	7	6	4.2	3.4
0	7	7	4.2	3.4
0	7	8	4.2	3.4
0	7	9	4.2	3.4
0	7	10	4.2	3.4
0	7	11	4.2	3.4
0	7	12	4.2	3.4
0	7	13	4.2	3.4
0	7	14	4.2	3.4
0	7	15	4.2	3.4
0	7	16	4.2	3.4
0	8	1	4.2	3.4
0	8	2	4.2	3.4
0	8	3	4.2	3.4
0	8	4	4.2	3.4
0	8	5	4.2	3.4
0	8	6	4.2	3.4
0	8	7	4.2	3.4
0	8	8	4.2	3.4
0	8	9	4.2	3.4
0	8	10	4.2	3.4
0	8	11	4.2	3.4
0	8	12	4.2	3.4
0	8	13	4.2	3.4
0	8	14	4.2	3.4
0	8	15	4.2	3.4
0	8	16	4.2	3.4
0	9	1	4.2	3.4
0	9	2	4.2	3.4
0	9	3	4.2	3.4
0	9	4	4.2	3.4
0	9	5	4.2	3.4
0	9	6	4.2	3.4
0	9	7	4.2	3.4
0	9	8	4.2	3.4
0	9	9	4.2	3.4
0	9	10	4.2	3.4
0	9	11	4.2	3.4
0	9	12	4.2	3.4
0	9	13	4.2	3.4
0	9	14	4.2	3.4
0	9	15	4.2	3.4
0	9	16	4.2	3.4
0	10	1	4.2	3.4
0	10	2	4.2	3.4
0	10	3	4.2	3.4
0	10	4	4.2	3.4
0	10	5	4.2	3.4
0	10	6	4.2	3.4
0	10	7	4.2	3.4
0	10	8	4.2	3.4
0	10	9	4.2	3.4
0	10	10	4.2	3.4
0	10	11	4.2	3.4
0	10	12	4.2	3.4
0	10	13	4.2	3.4
0	10	14	4.2	3.4
0	10	15	4.2	3.4
0	10	16	4.2	3.4
0	11	1	4.2	3.4
0	11	2	4.2	3.4
0	11	3	4.2	3.4
0	11	4	4.2	3.4
0	11	5	4.2	3.4
0	11	6	4.2	3.4
0	11	7	4.2	3.4
0	11	8	4.2	3.4
0	11	9	4.2	3.4
0	11	10	4.2	3.4
0	11	11	4.2	3.4
0	11	12	4.2	3.4
0	11	13	4.2	3.4
0	11	14	4.2	3.4
0	11	15	4.2	3.4
0	11	16	4.2	3.4
0	12	1	4.2	3.4
0	12	2	4.2	3.4
0	12	3	4.2	3.4
0	12	4	4.2	3.4
0	12	5	4.2	3.4
0	12	6	4.2	3.4
0	12	7	4.2	3.4
0	12	8	4.2	3.4
0	12	9	4.2	3.4
0	12	10	4.2	3.4
0	12	11	4.2	3.4
0	12	12	4.2	3.4
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0	4	8	6.2	5.3
0	4	9	12.1	12.7
0	4	11	9.7	10.4
0	4	12	8.5	9.7
0	4	13	12.5	11.6
0	4	14	4.1	4.1
0	4	15	7.0	7.2
0	4	16	5.1	5.3
0	4	19	3.5	3.9
0	4	0	6.5	4.4
0	4	0	16.2	15.7
0	4	0	7.4	8.1
0	4	0	34.0	24.7
0	4	0	9.2	7.0
0	4	0	5.7	5.8
0	4	0	8.5	8.1
0	4	0	7.5	7.6
1	4	1	15.7	16.2
1	4	2	4.9	4.2
1	4	3	4.1	3.6
1	4	4	20.0	16.5
1	4	5	23.6	20.3
1	4	6	13.9	13.9
1	4	7	18.0	16.5
1	4	8	5.1	5.3
1	4	9	6.3	6.9
1	4	10	5.5	6.6
1	4	11	6.2	7.9
1	4	13	6.9	7.7
1	4	14	5.0	5.0
1	4	16	7.0	6.8
1	4	18	4.1	4.3
2	4	1	14.8	11.9
2	4	2	11.0	7.9
2	4	3	29.4	14.7
2	4	4	8.1	7.7
2	4	6	6.6	6.1
2	4	7	12.6	13.0
2	4	8	8.0	6.1
2	4	9	6.4	5.7
2	4	10	6.1	6.6
2	4	11	14.2	14.7
2	4	12	8.9	8.9
2	4	13	7.3	6.8
2	4	14	6.3	5.0
2	4	15	4.1	3.7
2	4	16	10.8	10.2
2	4	17	3.9	3.9
2	4	18	3.7	3.4
2	4	19	3.4	3.4
2	4	20	3.4	3.4
3	4	1	28.5	23.6
3	4	2	25.5	18.8
3	4	3	15.8	14.5
3	4	4	15.9	13.7
3	4	5	7.9	8.0
3	4	6	17.5	18.0
3	4	7	11.6	12.0
3	4	8	10.2	10.4
3	4	9	5.1	5.1
3	4	10	4.8	4.8
3	4	12	8.4	8.1
3	4	13	6.2	6.0
3	4	15	6.7	6.7
3	4	16	4.3	4.6
4	4	1	28.5	23.6
4	4	2	25.5	18.8
4	4	3	15.8	14.5
4	4	4	15.9	13.7
4	4	5	7.9	8.0
4	4	6	17.5	18.0
4	4	7	11.6	12.0
4	4	8	10.2	10.4
4	4	9	5.1	5.1
4	4	10	4.8	4.8
4	4	12	8.4	8.1
4	4	13	6.2	6.0
4	4	15	6.7	6.7
4	4	16	4.3	4.6
5	4	1	13.6	11.7
5	4	2	10.8	9.7
5	4	3	12.7	9.0
5	4	4	10.9	8.7
5	4	5	13.6	11.7
5	4	6	8.7	7.8
5	4	7	8.1	7.9
5	4	8	9.9	10.7
5	4	9	20.9	18.2
5	4	10	4.8	3.5
5	4	11	11.8	10.3
5	4	12	12.5	8.6
5	4	13	6.2	6.0
5	4	14	8.4	8.1
5	4	15	13.7	11.3
5	4	16	8.0	6.4
5	4	17	6.6	6.6
5	4	18	3.3	2.6
6	4	1	17.5	10.7
6	4	2	32.4	21.9
6	4	3	19.9	14.1
6	4	4	12.7	9.1
6	4	5	7.7	9.1
6	4	6	16.8	16.1
6	4	7	16.2	16.5
6	4	8	18.1	18.0
6	4	9	5.6	6.2
6	4	10	10.1	8.8
6	4	11	6.8	7.4
6	4	13	4.0	3.6
6	4	16	2.0	2.7
6	4	17	5.8	4.7
7	4	1	19.4	14.4
7	4	2	20.7	14.5
7	4	3	12.8	8.9
7	4	4	19.2	17.2
7	4	5	21.1	18.3
7	4	6	10.6	11.1
7	4	7	7.2	7.2
7	4	8	4.9	3.9
7	4	9	7.6	8.7
7	4	10	5.2	6.6
7	4	11	7.6	8.1
7	4	12	8.9	10.7
8	4	1	4.9	3.9
8	4	2	6.8	5.9
8	4	3	27.3	23.2
8	4	4	10.8	10.2
8	4	5	5.3	6.0
5	4	-5	10.6	9.9
5	4	-6	6.3	7.2
5	4	-7	12.2	12.2
5	4	-8	18.8	16.0
5	4	-9	14.3	12.1
5	4	-10	9.0	9.9
5	4	-11	5.5	5.4
5	4	-12	7.1	6.3
5	4	-13	4.0	5.7
5	4	-14	7.7	7.4
5	4	-15	5.5	5.4
6	4	-1	13.7	11.5
6	4	-2	12.8	13.3
6	4	-3	4.7	4.5
6	4	-4	7.4	6.1
6	4	-5	6.2	6.0
6	4	-6	5.5	6.2
6	4	-7	4.2	4.5
6	4	-8	4.1	4.2
6	4	-9	4.1	4.4
6	4	-10	4.2	4.4
6	4	-11	4.4	5.4
6	4	-12	4.3	4.7
6	4	-13	4.1	4.1
6	4	-14	4.1	4.1
6	4	-15	4.2	4.2
7	4	-1	10.6	10.1
7	4	-2	5.1	5.1
7	4	-3	11.2	10.4
7	4	-4	12.8	10.4
7	4	-5	11.9	10.1
7	4	-6	11.9	12.2
7	4	-7	14.0	14.0
7	4	-8	16.4	16.6
7	4	-9	12.3	12.4
7	4	-10	6.5	6.5
7	4	-11	4.5	4.5
7	4	-12	5.1	5.1
7	4	-13	3.9	4.2
7	4	-14	4.6	4.3
7	4	-15	4.8	4.5
8	4	-1	5.7	4.6
8	4	-2	6.9	6.4
8	4	-3	4.2	4.1
8	4	-4	3.7	3.5
8	4	-5	2.7	2.7
8	4	-6	4.2	4.1
8	4	-7	8.0	5.7
8	4	-8	3.4	4.0
8	4	-9	2.1	4.2
8	4	-10	14.0	17.1
8	4	-11	23.8	23.4
8	4	-12	19.8	19.4
8	4	-13	7.6	6.2
8	4	-14	2.8	3.1
8	4	-15	5.6	5.6
8	4	-16	7.9	8.5
8	4	-17	6.3	6.0
8	4	-18	7.1	8.0
8	4	-19	7.7	7.7
8	4	-12	12.9	10.9
8	4	-13	6.8	6.4
8	4	-15	4.9	4.1
8	4	-16	6.9	7.0
8	4	-17	4.1	4.1
8	4	-20	4.8	4.2
9	4	-1	19.2	18.5
9	4	-2	5.1	5.8
9	4	-3	4.5	6.1
9	4	-5	20.4	17.1
9	4	-6	16.2	17.2
9	4	-7	10.9	10.6
9	4	-8	15.6	17.2
9	4	-9	13.1	12.0
9	4	-10	13.2	13.3
9	4	-11	9.8	10.9
9	4	-12	9.2	9.7
9	4	-13	8.3	10.1
9	4	-16	7.8	8.9
9	4	-17	6.6	6.6
9	4	-19	3.3	2.6
10	4	-1	17.5	10.7
10	4	-2	19.9	14.1
10	4	-3	12.7	9.1
10	4	-4	7.7	8.3
10	4	-5	10.4	9.9
10	4	-6	3.7	4.4
10	4	-7	8.3	9.9
10	4	-8	12.7	15.0
10	4	-10	4.4	3.7
10	4	-11	6.9	6.1
10	4	-12	4.9	5.0
10	4	-13	2.7	3.8
10	4	-14	11.9	13.9
10	4	-15	8.2	8.2
11	4	-1	10.1	10.0
11	4	-2	7.2	7.9
11	4	-3	5.1	5.1
11	4	-4	11.2	11.2
11	4	-5	10.4	11.1
0	5	1	10.8	14.7
0	5	2	7.3	10.6
0	5	3	5.3	6.0
0	5	4	3.8	3.4
0	5	5	9.3	12.2
0	5	6	5.3	8.0
0	5	7	5.2	6.3
0	5	9	6.2	8.7
0	5	10	7.3	9.0
0	5	11

TABLE 3.4

ORTHOGONAL COORDINATES IN Å ANGSTRØM AND E.S.D.s

ATOM	X'	Y	Z'
Br(1)	2.414 ± 2	1.513 ± 0	3.291 ± 2
O(1)	14.794 ± 13	2.254 ± 13	11.064 ± 10
O(2)	9.462 ± 11	1.315 ± 13	7.281 ± 10
O(3)	8.689 ± 10	2.869 ± 11	8.700 ± 10
O(4)	6.684 ± 13	1.163 ± 14	8.757 ± 13
C(1)	11.963 ± 12	1.492 ± 16	15.084 ± 12
C(2)	11.811 ± 15	1.449 ± 19	16.645 ± 14
C(3)	13.154 ± 18	1.017 ± 15	17.284 ± 14
C(4)	14.391 ± 14	1.790 ± 13	16.882 ± 13
C(5)	14.442 ± 12	1.897 ± 11	15.301 ± 12
C(6)	15.667 ± 13	2.639 ± 17	14.789 ± 15
C(7)	15.811 ± 14	2.356 ± 18	13.215 ± 15
C(8)	14.610 ± 14	2.797 ± 13	12.437 ± 14
C(9)	13.344 ± 14	2.114 ± 13	13.045 ± 13
C(10)	13.130 ± 12	2.381 ± 12	14.601 ± 12
C(11)	12.056 ± 15	2.335 ± 15	12.135 ± 14
C(12)	11.522 ± 15	1.021 ± 14	11.615 ± 14
C(13)	10.292 ± 14	1.135 ± 16	10.647 ± 14
C(14)	10.735 ± 13	1.865 ± 16	9.294 ± 14
C(15)	9.631 ± 15	1.918 ± 18	8.300 ± 14

C(16)	9.715 ± 19	-0.226 ± 17	10.341 ± 16
C(17)	14.557 ± 17	4.298 ± 20	12.310 ± 16
C(18)	14.432 ± 18	3.135 ± 16	17.621 ± 15
C(19)	15.670 ± 19	1.025 ± 16	17.387 ± 16
C(20)	12.782 ± 16	3.858 ± 13	14.841 ± 14
C(21)	7.619 ± 16	3.094 ± 18	7.792 ± 15
C(22)	6.613 ± 14	2.007 ± 16	7.843 ± 14
C(23)	5.581 ± 13	1.910 ± 16	6.754 ± 13
C(24)	4.783 ± 17	0.734 ± 20	6.594 ± 16
C(25)	3.870 ± 18	0.631 ± 18	5.623 ± 17
C(26)	3.690 ± 12	1.742 ± 23	4.696 ± 13
C(27)	4.438 ± 15	2.821 ± 22	4.816 ± 17
C(28)	5.360 ± 15	2.959 ± 19	5.824 ± 16

TABLE 3.5

PRINCIPAL VALUES OF VIBRATION TENSORS AND THEIR DIRECTION COSINES REFERRED TO ORTHOGONAL AXES

ATOM	$U(A)^{o2}$	D1	D2	D3
Br(1)	0.2091	-0.5295	0.7712	0.3533
	0.0542	0.7443	0.2226	0.6296
	0.1114	0.4069	0.5964	-0.6919
O(1)	0.1102	0.9987	-0.0147	0.0497
	0.0574	-0.0509	-0.0967	0.9940
	0.0601	-0.0098	-0.9952	-0.0974
O(2)	0.1133	-0.6548	-0.4916	0.5740
	0.0460	0.2860	0.5419	0.7903
	0.0544	-0.6996	0.6817	-0.2142
O(3)	0.0954	-0.7148	-0.3007	0.6314
	0.0328	0.0286	0.8895	0.4560
	0.0584	-0.6987	0.3440	-0.6273
O(4)	0.1442	-0.4416	0.4380	0.7830
	0.0516	-0.0061	-0.8742	0.4856
	0.0753	0.8972	0.2097	0.3887
C(1)	0.0709	0.0081	-0.5083	0.8611
	0.0369	0.5272	0.7340	0.4282
	0.0444	-0.8497	0.4505	0.2739
C(2)	0.0441	0.4509	0.8890	0.0800
	0.0742	0.8914	-0.4531	0.0116
	0.0656	0.0466	0.0661	-0.9967
C(3)	0.0996	-0.9988	0.0413	0.0253
	0.0341	-0.0390	-0.9955	0.0869
	0.0566	0.0288	0.0858	0.9959
C(4)	0.0949	-0.7538	0.0493	0.6552
	0.0134	-0.0624	-0.9980	0.0033
	0.0480	0.6541	-0.0384	0.7554
C(5)	0.0037	-0.0146	0.9975	0.0697
	0.0647	-0.6879	-0.0606	0.7232
	0.0495	0.7256	-0.0374	0.6871

C(6)	0.0769	-0.4183	-0.0188	0.9081
	0.0353	0.9027	0.1019	0.4180
	0.0561	-0.1004	0.9946	-0.0257
C(7)	0.0436	-0.7913	-0.5655	0.2324
	0.0718	-0.5319	0.8242	0.1946
	0.0614	-0.3016	0.0304	-0.9530
C(8)	0.0121	-0.0393	0.9992	0.0105
	0.0704	0.4197	0.0069	0.9076
	0.0570	0.9068	0.0400	-0.4197
C(9)	0.0763	-0.6982	-0.0175	0.7157
	0.0183	0.1276	-0.9867	0.1004
	0.0437	0.7044	0.1614	0.6912
C(10)	0.0638	-0.5897	-0.0343	0.8069
	0.0158	-0.0466	0.9989	0.0084
	0.0378	-0.8063	-0.0326	-0.5907
C(11)	0.0762	-0.7342	-0.1060	0.6706
	0.0320	0.2093	-0.9750	0.0751
	0.0500	0.6459	0.1955	0.7380
C(12)	0.0803	-0.8663	0.0651	0.4952
	0.0289	-0.0611	-0.9978	0.0244
	0.0505	0.4957	-0.0091	0.8684
C(13)	0.0772	-0.7042	0.0699	0.7066
	0.0348	0.5678	0.6529	0.5013
	0.0529	-0.4263	0.7542	-0.4995
C(14)	0.0663	-0.6064	0.1026	0.7885
	0.0460	0.4952	0.8246	0.2736
	0.0534	-0.6221	0.5564	-0.5508
C(15)	0.0683	-0.8348	0.4500	0.3170
	0.0543	0.1998	-0.2889	0.9363
	0.0603	0.5129	0.8450	0.1513
C(16)	0.1250	-0.8347	0.3911	0.3878
	0.0215	0.4563	0.8853	0.0893
	0.0686	-0.3085	0.2515	-0.9174
C(17)	0.1022	0.8634	-0.4098	0.2942
	0.0472	-0.4534	-0.8861	0.0965
	0.0658	0.2212	-0.2167	-0.9509

C(18)	0.1135	-0.8961	0.0288	0.4429
	0.0190	0.1661	0.9472	0.2744
	0.0651	-0.4116	0.3195	-0.8535
C(19)	0.0228	0.2523	-0.9093	0.3309
	0.1201	-0.8906	-0.0845	0.4469
	0.0727	-0.3784	-0.4075	-0.8311
C(20)	0.0102	-0.0671	0.9872	0.1449
	0.0959	-0.9122	-0.1195	0.3918
	0.0544	0.4041	-0.1059	0.9085
C(21)	0.0809	-0.7538	-0.0250	0.6566
	0.0484	0.5901	0.4140	0.6931
	0.0585	-0.2892	0.9099	-0.2973
C(22)	0.0382	0.6230	-0.6959	0.3572
	0.0717	-0.2576	0.2485	0.9337
	0.0550	-0.7386	-0.6737	-0.0245
C(23)	0.0380	-0.7213	0.6879	0.0812
	0.0648	0.6387	0.6151	0.4622
	0.0575	0.2680	0.3852	-0.8830
C(24)	0.0763	0.6987	-0.7104	0.0844
	0.0668	-0.1970	-0.0776	0.9773
	0.0694	-0.6878	-0.6995	-0.1942
C(25)	0.0502	0.1080	0.8428	0.5274
	0.0803	0.4450	-0.5153	0.7324
	0.0666	0.8890	0.1556	-0.4307
C(26)	0.0150	0.7385	0.0912	0.6681
	0.1195	-0.0770	-0.9729	0.2180
	0.0816	0.6698	-0.2124	-0.7115
C(27)	0.1109	-0.3591	0.6777	0.6417
	0.0388	0.9056	0.0866	0.4153
	0.0669	0.2259	0.7302	-0.6448
C(28)	0.0796	-0.2348	0.4261	0.8737
	0.0529	-0.2599	-0.8936	0.3660
	0.0603	0.9367	-0.1411	0.3205

TABLE 3.6

MOLECULAR DIMENSIONS

(a) Bond lengths and e.s.d.'s

C(1) -C(2)	1.569 ± 19 Å	C(22)-C(23)	1.504 ± 19 Å
C(1) -C(10)	1.545 ± 18		
C(2) -C(3)	1.548 ± 23	C(23)-C(24)	1.430 ± 25
C(3) -C(4)	1.514 ± 22	C(23)-C(28)	1.420 ± 23
C(4) -C(5)	1.586 ± 18	C(24)-C(25)	1.337 ± 24
C(4) -C(18)	1.535 ± 21	C(25)-C(26)	1.458 ± 26
C(4) -C(19)	1.574 ± 23	C(26)-C(27)	1.319 ± 28
C(5) -C(6)	1.521 ± 18	C(27)-C(28)	1.373 ± 22
C(6) -C(7)	1.606 ± 21		
C(7) -C(8)	1.498 ± 20	C(15)-O(2)	1.196 ± 19
C(8) -C(9)	1.562 ± 19		
C(8) -C(17)	1.507 ± 24	C(22)-O(4)	1.246 ± 20
C(9) -C(10)	1.593 ± 18		
C(9) -C(11)	1.593 ± 20	C(15)-O(3)	1.398 ± 19
C(10)-C(20)	1.536 ± 18		
C(11)-C(12)	1.511 ± 21	C(21)-O(3)	1.420 ± 19
C(12)-C(13)	1.569 ± 20	C(8) -O(1)	1.488 ± 17
C(13)-C(16)	1.510 ± 23		
C(13)-C(14)	1.600 ± 20	Br-C(26)	1.912 ± 13
C(14)-C(15)	1.487 ± 20		
C(21)-C(22)	1.481 ± 23		

(b) Bond angles and e.s.d.'s

C(2) -C(1) -C(10)	113.6 ± 1.1°	C(9) -C(11)-C(12)	111.2 ± 1.2°
C(1) -C(2) -C(3)	109.5 ± 1.1	C(11)-C(12)-C(13)	115.2 ± 1.2
C(2) -C(3) -C(4)	117.2 ± 1.3	C(12)-C(13)-C(16)	111.1 ± 1.3
C(3) -C(4) -C(5)	109.0 ± 1.1	C(12)-C(13)-C(14)	109.7 ± 1.1
C(3) -C(4) -C(18)	110.0 ± 1.2	C(16)-C(13)-C(14)	110.2 ± 1.2
C(3) -C(4) -C(19)	109.3 ± 1.2	C(13)-C(14)-C(15)	112.1 ± 1.2
C(5) -C(4) -C(18)	114.9 ± 1.1	O(3) -C(21)-C(22)	111.9 ± 1.3
C(5) -C(4) -C(19)	109.1 ± 1.1		
C(18)-C(4) -C(19)	104.5 ± 1.2	C(15)-O(3) -C(21)	115.6 ± 1.1
C(4) -C(5) -C(6)	113.2 ± 1.0		
C(4) -C(5) -C(10)	116.2 ± 1.0	O(2) -C(15)-O(3)	119.4 ± 1.3
C(6) -C(5) -C(10)	112.0 ± 1.0	O(2) -C(15)-C(14)	131.1 ± 1.5
C(5) -C(6) -C(7)	108.4 ± 1.1	O(3) -C(15)-C(14)	109.5 ± 1.2
C(6) -C(7) -C(8)	112.7 ± 1.2		
O(1) -C(8) -C(7)	105.8 ± 1.1	O(4) -C(22)-C(21)	118.9 ± 1.3
O(1) -C(8) -C(9)	107.5 ± 1.1	O(4) -C(22)-C(23)	121.7 ± 1.4
O(1) -C(8) -C(17)	106.9 ± 1.1	C(21)-C(22)-C(23)	119.3 ± 1.3
C(7) -C(8) -C(9)	108.6 ± 1.1		
C(7) -C(8) -C(17)	111.4 ± 1.3	C(22)-C(23)-C(24)	121.1 ± 1.4
C(9) -C(8) -C(17)	116.1 ± 1.2	C(22)-C(23)-C(28)	122.2 ± 1.4
C(8) -C(9) -C(10)	114.5 ± 1.1	C(24)-C(23)-C(28)	116.6 ± 1.3
C(8) -C(9) -C(11)	111.9 ± 1.1	C(23)-C(24)-C(25)	121.7 ± 1.7
C(10)-C(9) -C(11)	115.3 ± 1.1	C(24)-C(25)-C(26)	119.2 ± 1.7
C(1) -C(10)-C(5)	108.4 ± 1.0	Br -C(26)-C(25)	117.3 ± 1.4
C(1) -C(10)-C(9)	108.1 ± 1.0	Br -C(26)-C(27)	122.9 ± 1.4
C(1) -C(10)-C(20)	109.5 ± 1.1	C(25)-C(26)-C(27)	119.7 ± 1.4
C(5) -C(10)-C(9)	105.9 ± 1.0	C(26)-C(27)-C(28)	122.0 ± 1.8
C(5) -C(10)-C(20)	114.7 ± 1.0	C(23)-C(28)-C(27)	120.7 ± 1.7
C(9) -C(10)-C(20)	110.1 ± 1.0		

TABLE 3.7

NON-BONDED DISTANCES

(a) Some intramolecular distances

C(4) ...C(10)	2.67 Å
C(8) ...C(10)	2.65
C(20)...C(17)	3.12
C(20)...C(18)	3.31
C(20)...C(1)	2.52
C(20)...C(9)	2.57
C(20)...C(5)	2.61
C(18)...C(3)	2.50
C(18)...C(5)	2.63
C(17)...C(7)	2.48
C(17)...C(9)	2.60
C(18)...C(19)	2.46
C(16)...C(15)	2.96
C(16)...O(2)	3.44
C(16)...O(3)	3.65
C(16)...O(4)	3.69
C(14)...C(11)	3.17
C(14)...O(2)	3.61
C(15)...C(22)	3.05
C(15)...O(4)	3.08
O(4) ...O(3)	2.63
O(4) ...O(2)	3.15
O(4) ...C(24)	2.91
C(21)...C(28)	3.00

(b) Intermolecular distances <4.0 Å

Atom A	Atom B	Equivalent position* of Atom B	Cell of Atom B	Distance
Br	...C(20)	II	(0,-1, 0)	3.85 Å
O(1)	...O(2)	II	(1, 0, 0)	3.25
O(1)	...C(21)	II	(1,-1, 0)	3.37
O(1)	...C(28)	II	(1,-1, 0)	3.58
O(1)	...C(24)	II	(1, 0, 0)	3.81
O(1)	...C(23)	II	(1, 0, 0)	3.92
O(2)	...C(17)	II	(1,-1, 0)	3.49
O(2)	...C(14)	II	(1,-1, 0)	3.61
O(2)	...C(11)	II	(1,-1, 0)	3.91
O(2)	...C(8)	II	(1,-1, 0)	3.94
O(3)	...C(16)	I	(0, 1, 0)	3.53
O(3)	...C(24)	II	(0, 0, 0)	3.62
O(4)	...C(22)	II	(0,-1, 0)	3.27
O(4)	...C(21)	II	(0,-1, 0)	3.48
O(4)	...C(23)	II	(0,-1, 0)	3.58
O(4)	...O(4)	II	(0,-1, 0)	3.66
O(4)	...O(4)	II	(0, 0, 0)	3.66
O(4)	...C(24)	II	(0, 0, 0)	3.80
O(4)	...C(28)	II	(0,-1, 0)	3.81
C(1)	...C(20)	I	(0,-1, 0)	3.78
C(16)	...C(25)	II	(0,-1, 0)	3.76
C(16)	...C(26)	II	(0,-1, 0)	3.83
C(16)	...C(24)	II	(0,-1, 0)	3.90
C(17)	...C(28)	II	(1, 0, 0)	3.81
C(17)	...C(23)	II	(1, 0, 0)	3.89
C(21)	...C(24)	II	(0, 0, 0)	3.93
C(25)	...C(27)	I	(0,-1, 0)	3.99

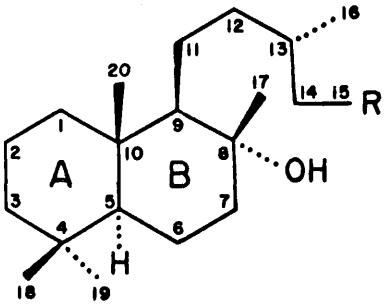
*The equivalent positions are: I (x, y, z)

II (1-x,½+y,1-z)

Atom A is in equivalent position I in the cell (0,0,0).

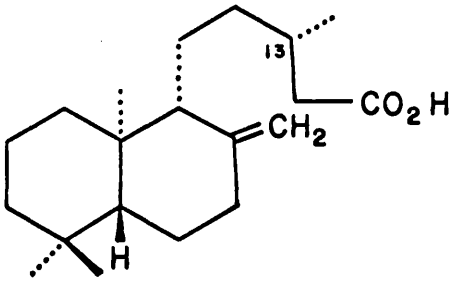
6. Description and discussion of the structure

Since the absolute configuration of labdanolic acid is known this X-ray analysis of p-bromophenacyl labdanolate (II) unambiguously establishes that the configuration at C(13) is (S). Consequently it is also (S) in labdanolic (III) and eperuic (IV) acids and not (R) as previously reported. It also confirms the validity of structure I proposed for labdanolic acid by Cocker and Halsall (1956b).



II; R = $CO_2 \cdot CH_2 \cdot CO \cdot C_6H_4Br$

III; R = CO_2H



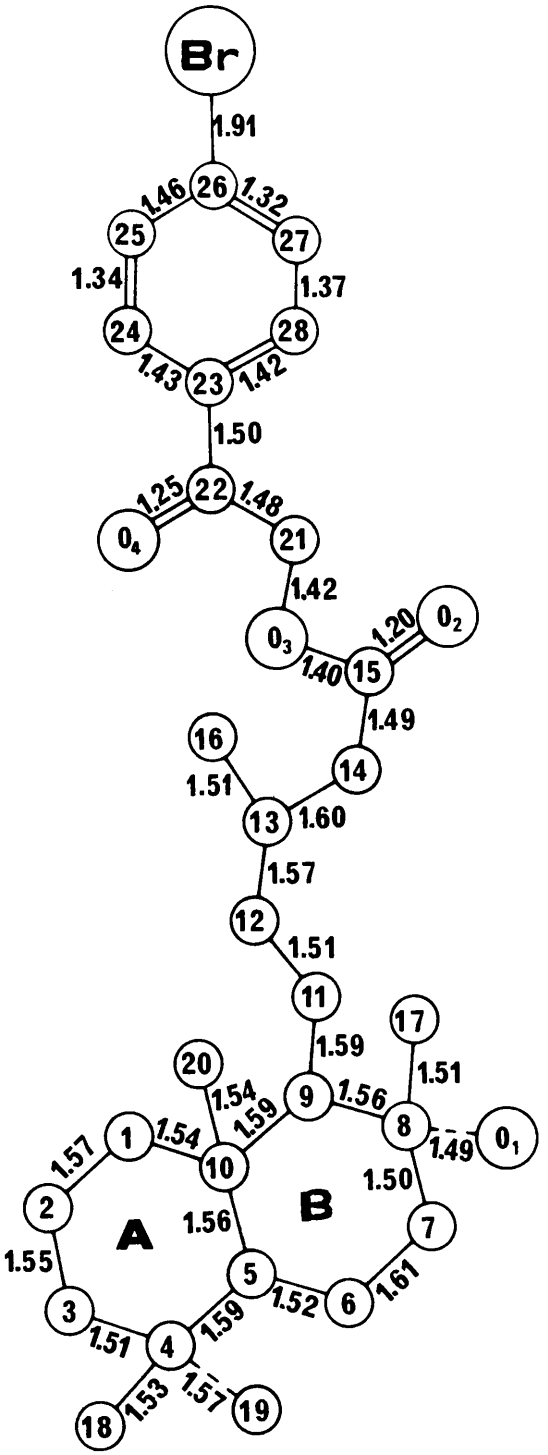
IV

The configuration of the molecule can best be seen from Figure 3.2. The bond lengths and angles are shown in Figure 3.3 and the least-squares planes are listed in

Figure 3.3

a) Bond lengths

b) Bond angles


Br
1.91
26
1.46
1.32
25
27
1.34
1.37
24
28
1.43
23
1.42
1.50
22
1.25
1.48
O_4
21
1.42
O_3
1.20
O_2
1.40
15
1.49
16
14
1.51
13
1.60
1.57
12
1.51
11
17
1.59
1.51
20
1.54
9
1.56
8
1.59
1.49
O_1
1
1.54
1.57
10
1.50
2
A
B
7
1.56
1.55
5
1.61
3
1.52
6
1.59
1.51
4
1.53
1.57
18
19

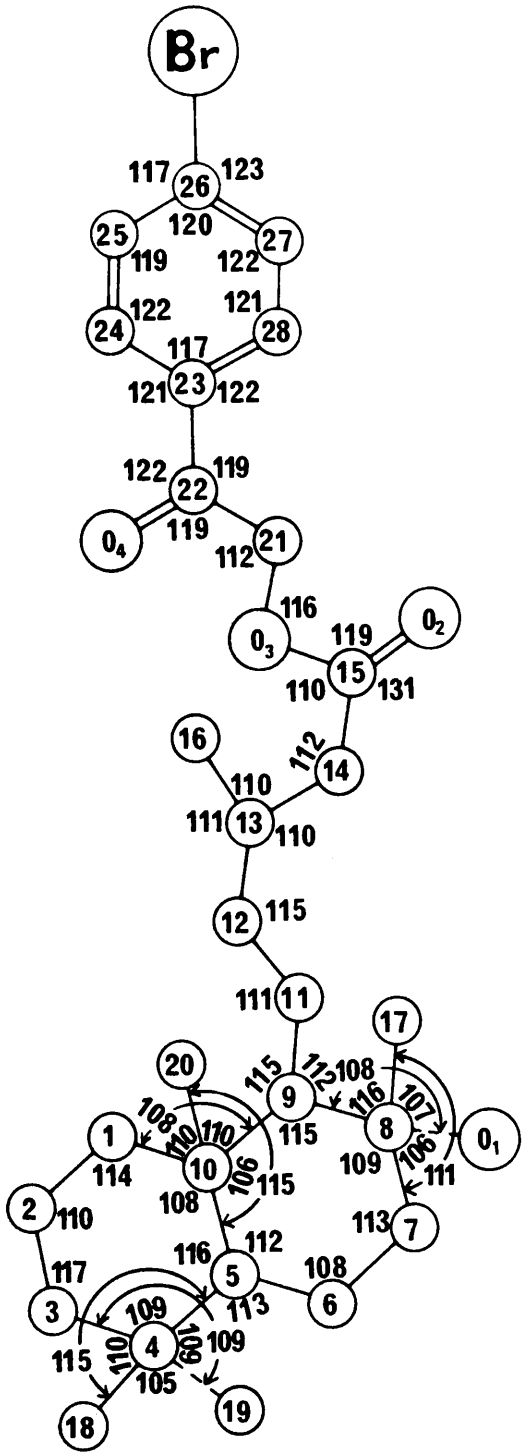

Br
26
25
27
24
28
23
22
21
O_4
O_3
O_2
15
16
14
13
12
11
17
20
9
8
O_1
1
10
2
7
5
3
6
4
18
19

Table 3.8.

The two six-membered rings in the decalin system, *trans*-fused to each other, adopt slightly distorted chair conformations. Four carbon atoms of ring A (C(2), C(3), C(5), and C(10)) are coplanar and carbon atoms C(1) and C(4) are displaced from this plane by -0.66 and +0.61 Å, respectively. In a cyclohexane chair with all angles tetrahedral these two atoms would each have been displaced by 0.73 Å (calculated value). In ring B the atoms C(7), C(8), C(10), and C(5) are coplanar and the two atoms C(6) and C(9) are displaced from this plane by +0.73 and -0.68 Å, respectively. These two cyclohexane planes are not parallel to each other, as would have been expected in a regular *trans*-decalin system. The dihedral angle between them is 10°. The distortions are due to a bending of the axial methyl carbon atoms (C(17), C(18), and C(20)) away from each other. This diminishes the 1,3-diaxial interactions. The bending can best be illustrated by a comparison of the non-bonded distances C(4)...C(10) (2.67 Å) and C(8)...C(10) (2.65 Å) with the much longer ones C(18)...C(20) (3.31 Å) and C(17)...C(20) (3.12 Å). They are in good agreement with the corresponding distances in taxadienetetraol, the structure described in the previous chapter.

TABLE 3.8

LEAST-SQUARES PLANES

Plane 1
Ring A

Atom	Δ(Å)
C(2)	-0.005
C(3)	0.005
C(5)	-0.005
C(10)	0.005
C(1)*	-0.659
C(4)*	0.609

$\overline{\Delta^2}$ = 0.005
χ^2 = 0.5

Plane 2
Ring B

Atom	Δ(Å)
C(7)	0.012
C(8)	-0.011
C(10)	0.011
C(5)	-0.011
C(6)*	0.732
C(9)*	-0.678

$\overline{\Delta^2}$ = 0.011
χ^2 = 2.9

Plane 3
Carbon Chain

Atom	Δ(Å)
C(9)	0.018
C(11)	-0.016
C(12)	-0.020
C(13)	0.018
C(16)*	-0.184
C(6)*	0.066

$\overline{\Delta^2}$ = 0.018
χ^2 = 6.5

Plane 4
Ester Group

Atom	Δ(Å)
O(2)	-0.005
O(3)	-0.034
C(14)	0.022
C(15)	-0.010
C(21)	0.028
C(22)*	-1.271
C(13)*	-1.394

$\overline{\Delta^2}$ = 0.022
χ^2 = 16.4

Plane 5
Carbonyl Group

Atom	Δ(Å)
C(21)	-0.005
C(22)	0.017
C(23)	-0.005
O(4)	-0.007
O(3)*	-0.289

$\overline{\Delta^2}$ = 0.010
χ^2 = 1.8

Plane 6
Phenyl Ring

Atom	Δ(Å)
C(22)	-0.008
C(23)	0.008
C(24)	-0.002
C(25)	0.001
C(26)	0.003
C(27)	-0.015
C(28)	0.013
Br*	-0.055
O(4)*	0.162
C(21)*	-0.305

$\overline{\Delta^2}$ = 0.009
χ^2 = 2.4

*These atoms were not used to calculate the least-squares plane.

Plane	Equations for the least-squares planes
1	0.079 X' + 0.889 Y + 0.451 Z' = 9.740 Å
2	0.167 X' + 0.938 Y + 0.305 Z' = 8.857
3	0.601 X' + 0.073 Y - 0.796 Z' = -2.218
4	0.514 X' + 0.695 Y - 0.502 Z' = 2.130
5	- 0.611 X' + 0.571 Y + 0.549 Z' = 1.392
6	- 0.691 X' + 0.395 Y + 0.605 Z' = 0.976

(X', Y, Z' (in Å) are referred to the orthogonal axes a*, b, c, i.e. $X' = X\sin\beta$ and $Z' = Z + X\cos\beta$).

The carbon atoms C(9), C(11), C(12), C(13), and C(16) form a fully extended chain. The first four atoms are coplanar but C(16) is displaced from the plane by -0.18 Å. This plane is almost perpendicular to the ring-B plane (the dihedral angle between them is 86°).

A least-squares plane through the ester-group atoms (O(2), O(3), C(14), C(15)) and atom C(21) was calculated. With a χ^2 value of 16.4 these atoms are not strictly coplanar at a 0.1% significance level. However, in view of the following discussion where an increase in the e.s.d.'s of 50% is assumed they are in fact coplanar. The dihedral angle between the ester group and the extended carbon chain is 41°. A Newman projection down the C(14)-C(13) bond shows that the arrangement is very close to staggered, with C(12) *anti* to C(15) (Figure 3.4). The relevant dihedral angles are marked in this figure.

From a survey of a few crystal structures Mathieson (1965) found that in esters of primary alcohols the two hydrogen atoms attached to the alcohol α-carbon (here C(21)) were in a staggered relation to the double-bonded oxygen of the ester group (here O(2)). He suggested that this configuration would be energetically favoured. In fact, the arrangement found in this structure (Figure 3.5) corresponds to a rotation about the C(21)-O(3) bond by 112°

Figure 3.4

A Newman projection down the C(14)-C(13) bond.

Figure 3.5

A Newman projection down the C(21)-O(3) bond.

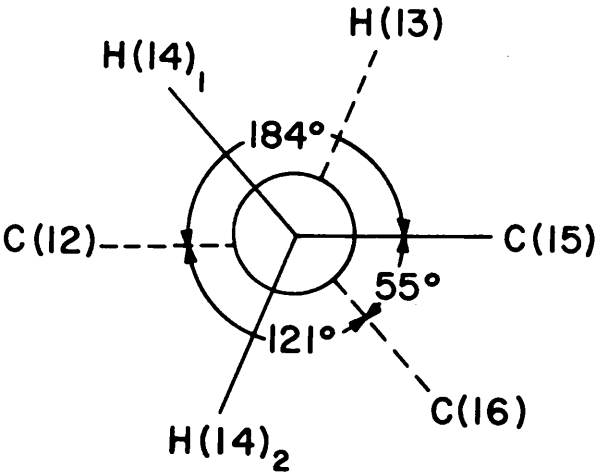


Fig. 3.4

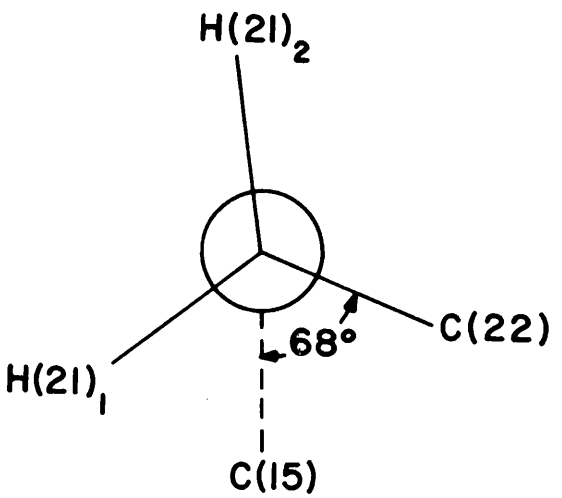


Fig. 3.5

from the position predicted by Mathieson. Thus C(15) is *anti* to one of the C(21) hydrogen atoms instead of being *anti* to C(22). The ester plane makes a dihedral angle of 79° with the carbonyl plane, defined by the atoms C(21), C(22), C(23), and O(4).

The atoms of the aromatic ring and atom C(22) are coplanar; the bromine atom is displaced from this plane by 0.055 Å. The carbonyl plane is rotated about the C(23)-C(22) bond so that the dihedral angle with the aromatic plane is 12°. As was noted in the previous chapter, such dihedral angles are not uncommon.

There are three bond lengths in this structure, Br-C(26) (1.912 Å), C(8)-O(1) (1.488 Å), and C(6)-C(7) (1.606 Å), which differ significantly at a 0.1% level from the values (1.85 ± 0.01, 1.426 ± 0.005, and 1.537 ± 0.005 Å) given by Sutton (1965). There are no obvious explanations for these deviations. Since the block-diagonal approximation was used in the least-squares refinement, the e.s.d.'s are likely to be underestimated. It seems reasonable to increase them by 50% and this is assumed in the following discussion. In view of this, none of the above-mentioned deviations in bond lengths are significant.

Some of the angles in the decalin system deviate

from normal values. In accordance with the theoretical calculations by Bucourt and Heinaut (1965) angles are considered normal in the range of 109.5 - 111.0° depending on the degree of substitution. All the deviations in this structure can be attributed to the previously mentioned bending of the 1,3 diaxial methyl groups away from each other, such as the large values of the angles C(5)-C(4)-C(18) (115°), C(9)-C(8)-C(17) (116°), and C(5)-C(10)-C(20) (115°). There is a general tendency to increased valency angles around the atoms adjacent to C(4), C(8), and C(10), even though only the angle C(4)-C(5)-C(10) (116°) is increased significantly. This is an effect of the same bending. The angles around the fully substituted carbon atoms C(4), C(8), and C(10), except those mentioned above, are approximately tetrahedral or slightly smaller. This agrees with the observations of Geise, Altona, and Romers (1967).

In un-ionised carboxylic groups two of the angles are usually about 125° and one approximately tetrahedral (Hahn, 1957). The angles around C(15) conform approximately to this pattern. The angles around C(22) are equal to 120° within experimental error.

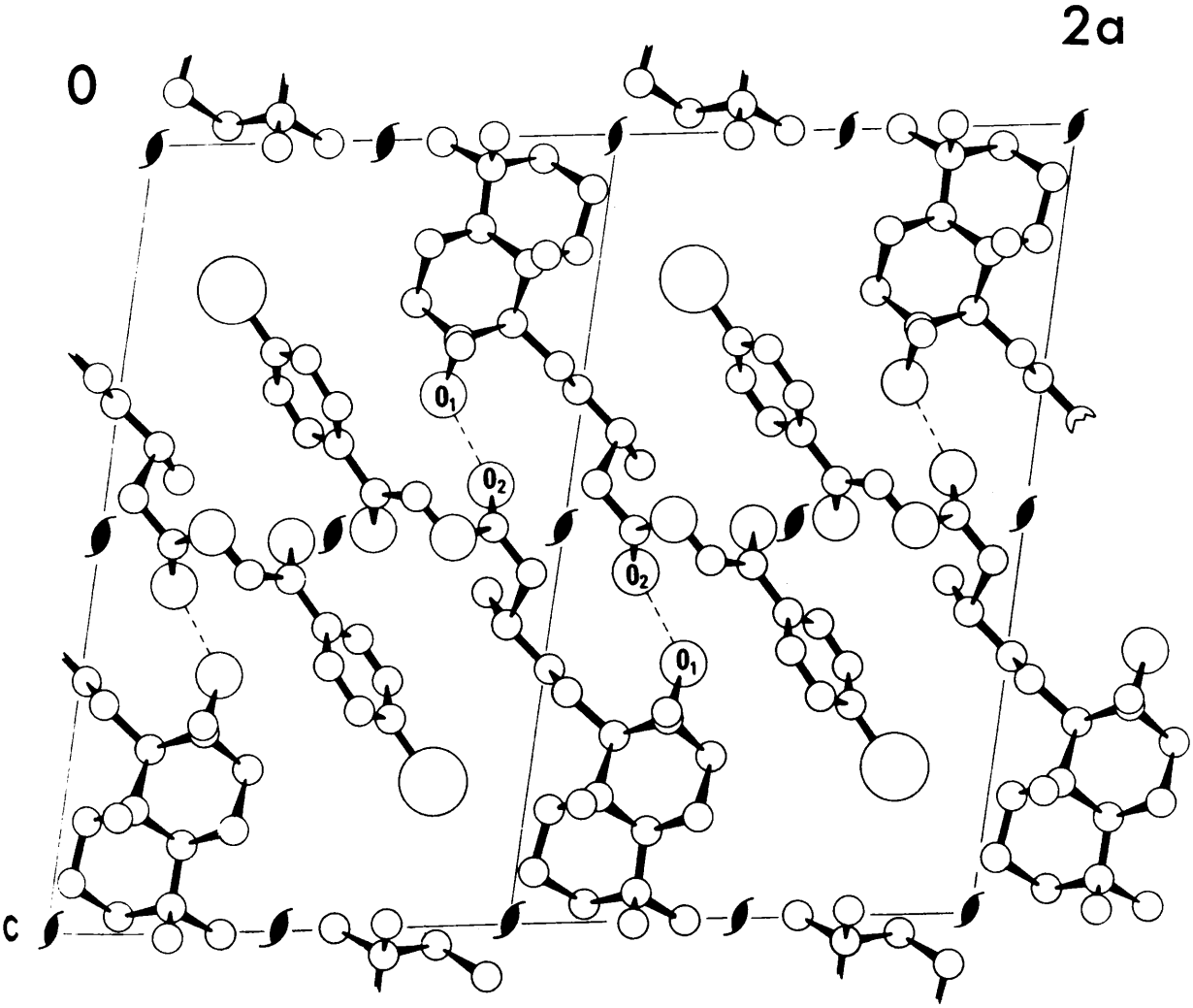
It has been reported (Baker *et al*, 1962) that intramolecular hydrogen bonding occurs in compounds of the

labdane type (methyl labdanolate, labdane-8α, 15-diol monoacetate, and labdane-8α, 15-diol) in very dilute solutions in carbon tetrachloride. On the basis of infrared spectroscopy it was suggested that this hydrogen bonding involves "closure" of a ten-membered ring (i.e. O(1)-H... O(2) or O(1)-H...O(3)). There is no such intramolecular hydrogen bond in this crystal structure. The hydrogen atom of the hydroxyl group could not be located from a difference Fourier map but it is probably involved in an extremely weak intermolecular hydrogen bond. The angle $C(8)\text{-}O(1)_{I}\ldots O(2)_{II}$ (106.7 ± 0.8°) is favourable for such a bond--even though the distance $O(1)_{I}\ldots O(2)_{II}$ is rather long (3.246 ± 0.017 Å). The value of the $C(8)\text{-}O(1)_{I}\ldots O(2)_{II}$ angle suggests that the hydroxyl hydrogen atom is located on the line connecting $O(1)_{I}$ and $O(2)_{II}$ so that the hydrogen bond is linear.

The arrangement of the molecules viewed along the b-axis can be seen in Figure 3.6 where the suggested hydrogen bond is marked with a broken line. The broken lines $O(1)_{I}\ldots O(2)_{II}$ and $O(2)_{I}\ldots O(1)_{II}$ from the molecule in equivalent position I do not go to the same molecule in equivalent position II. The former goes to the molecule at y+½ relative to equivalent position I, and the latter to the molecule at y-½. The molecules are thus

Figure 3.6

A packing diagram viewed along the b-axis.


2a
0
O_1
O_2
O_2
O_1
c

arranged as separate right-handed spirals around one of the two-fold screw axes (at $x = 0$, $z = \frac{1}{2}$) in each unit cell. The fact that p-bromophenacyl labdanolate crystallises as very long needles with the needle axis parallel to the b-axis can be easily understood from the molecular arrangement.

There are no other short intermolecular distances (Table 3.7) besides the one mentioned above.

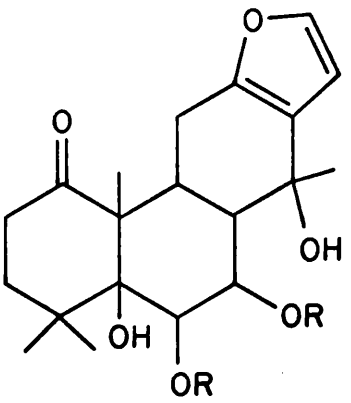
CHAPTER IV

The Crystal and Molecular Structure of a p-Bromobenzoate Derivative of ε-Caesalpin

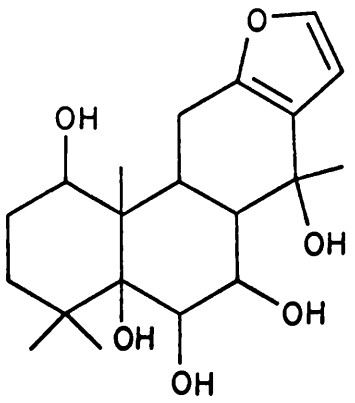
1. Introduction

Caesalpinia bonducella (Fleming) is a wild plant abundantly available in East Pakistan. The entire plant is used medicinally by local people. From the seeds of this plant Qudrat-i-Khuda and Ali (1963) isolated the bitter constituents α-, β-, and γ-caesalpins and determined their functional groups. The amorphous γ-caesalpin gave on hydrolysis a crystalline bitter compound, later called δ-caesalpin, together with acetic and myristic acids. From chemical studies Canonica, Jommi, Manitto, Pagnoni, and Pelizzoni (1966) showed the structures of α-, β-, and δ-caesalpins to be I, II, and III, respectively. The same authors also reported that γ-caesalpin is a δ-caesalpin ester of acetic and myristic acids.

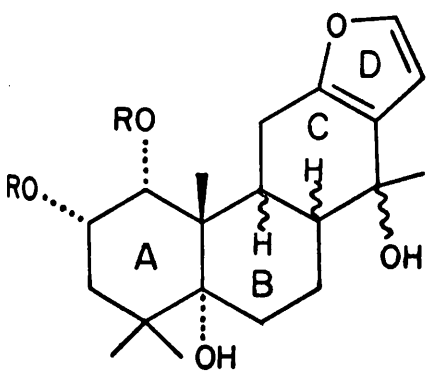
A new crystalline compound, ε-caesalpin $C_{24}H_{34}O_7$, was recently isolated from the seeds of *Caesalpinia bonducella*. Based on chemical and spectroscopic evidence the structure IV, or its enantiomer, was assigned to it (Balmain, Bjåmer, Connolly, and Ferguson, 1967). This X-ray analysis was undertaken in order to determine the complete structure and the absolute configuration of



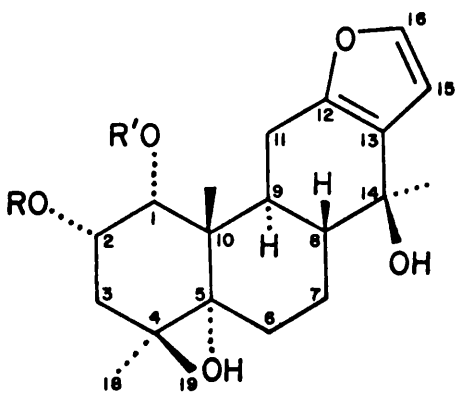
I ; R = Ac
II ; R = H



III



IV ; R = Ac
V ; R = H



VI ; R = p - Br · C_6H_4 · CO , R' = H
VII ; R = R' = Ac

ε-caesalpin. In order to obtain a derivative suitable for such an analysis, ε-caesalpin was treated with $LiAlH_4$ to give the tetraol (V) which was then esterified with p-bromobenzoyl chloride. The mono-p-bromobenzoate (VI), isolated by thin-layer chromatography, was used in this X-ray crystal structure determination.

2. Crystal data

1,2-Desacetyl-ε-caesalpin-2-p-bromobenzoate, $C_{27}H_{33}O_6Br$, F.W. = 533.2, m.p. = 169-170°C. Monoclinic, a = 6.563 ± 0.002, b = 12.999 ± 0.002, c = 14.809 ± 0.002 Å, β = 94.50 ± 0.03°, V = 1259.5 ± 0.5 $Å^3$ from Cu $K\alpha_1$ (λ = 1.54051 Å) and Cu $K\alpha_2$ (λ = 1.54433 Å). D_m = 1.403 $g.cm.^{-3}$ (by flotation in aqueous potassium iodide), Z = 2, D_x = 1.406 $g.cm.^{-3}$. F(000) = 556. Space group $P2_1$ (No. 4). Linear absorption coefficient μ = 27.8 $cm.^{-1}$ for Cu Kα radiation (λ = 1.5418 Å).

3. Crystallographic measurements

The material was crystallised from an acetone-ether solution. The crystals were colourless, very soft plates with (001) as the predominant face and they could not be cut without being destroyed. They are stable in the air.

The cell dimensions were obtained by a least-squares method proposed by Speakman (1966) from Okℓ and hOℓ

Weissenberg photographs calibrated with Al powder lines. The space group was determined from the absences (0k0 absent when k is odd) and from knowing that the parent ε-caesalpin is optically active ($[\alpha]_D = +2°$). Non-integrated equi-inclination Weissenberg data were collected with Ni-filtered Cu Kα radiation, using the multiple-film technique. The crystals deteriorated somewhat after 2-3 weeks of exposure in the X-ray beam. Two crystals of the same size (0.35 × 0.35 × 0.10 mm.), mounted along the crystallographic a and b axes, were used. From one crystal the layers 0kℓ through 6kℓ were obtained, and from the second one the layers h0ℓ and h1ℓ. The intensities were measured visually with a calibrated intensity strip and 2399 reflexions were obtained from the a-mounting and 460 reflexions (91 of which had not been measured previously) from the b-mounting. Another 256 reflexions which were too weak to be measured were included in the data with intensities ½ I_{min}. Out of the total number of reflexions (3115) 2728 are independent ones and represent 95% of the reflexions accessible within the Cu sphere. The intensities were corrected for Lorentz and polarisation factors but no absorption correction was applied.

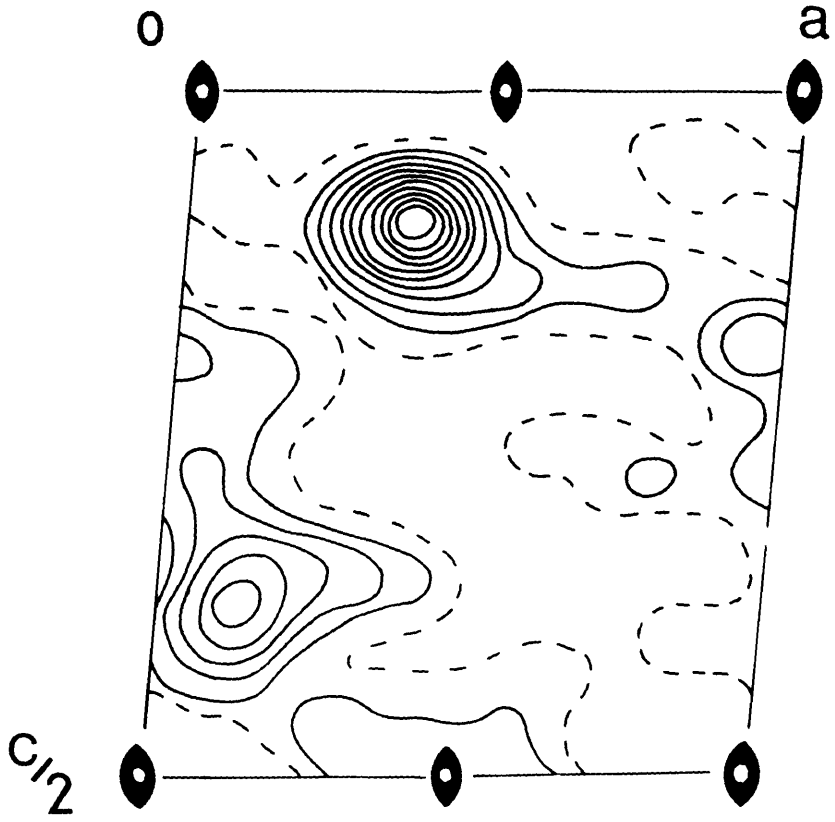
4. Structure determination

The structure was solved by the heavy-atom method; the

ratio $\Sigma f_H^2/\Sigma f_L^2$ = 0.88 at sinθ = 0. The three-dimensional data were sharpened to point atom with regard to bromine and the Harker section at v = ½ was calculated (Figure 4.1). The symmetry of the Patterson vector distribution is P2/m and it will contain a vector peak of double weight at (2x,½,2z) from symmetry-related atoms. The highest peak in the Harker section was interpreted as the Br-Br vector peak and the position of the bromine atom was determined to be (by Booth's (1948b) interpolation method): x = 0.1863, z = 0.0482; its y coordinate was chosen as ½. A structure-factor calculation with the bromine atom in this position gave an R-factor of 47%. Since the space group is polar in the y direction the first electron-density map, based on observed structure factors and bromine phase angles, contained pseudo-mirror planes parallel to (010) at y = 0, ½, 1, etc. However, it was possible to locate the benzoate group and carbon atom C(2) from it. In a subsequent structure-factor calculation based on bromine and the additional ten atoms the R-factor was lowered to 41%. From the second Fourier map the remaining atoms were located and with all the atoms included the R-factor was 27.7%. All the oxygen atoms had so far been treated as carbon atoms, but in the third Fourier map five of the peaks could be identified as oxygen atoms due to their

Figure 4.1

The Harker section at $v = \frac{1}{4}$. Contours are drawn at arbitrary intervals.


0
a
c/2

peak heights. During the structure-factor calculations an overall isotropic temperature factor of U = 0.05 $\mathring{A}^2$ was applied, and the data were put on an approximate absolute scale by making $k \sum_{hk\ell} |F_o| = \sum_{hk\ell} |F_c|$ for each layer.

5. Structure refinement

Coordinates, thermal parameters, and individual layer-scale factors were refined by the block-diagonal approximation of the least-squares method, minimising the expression $\sum_{hk\ell} w(|F_o| - |F_c|)^2$. The y coordinate of the bromine was held constant throughout the refinement.

One oxygen atom (O(5)) was first refined as a carbon atom, but after the first cycle of isotropic least squares it was recognised as an oxygen atom because of a large drop (0.014 $\mathring{A}^2$) in the U_{iso} value. After ten cycles of isotropic refinement R was lowered to 17.8%. During the structure determination and isotropic refinement only the data collected from the a-axis mounting had been included. The data from the b-axis mounting were added at the beginning of the anisotropic refinement. The common reflexions were not averaged; they were treated by the least-squares programme as independent observations. Eight cycles of anisotropic refinement were carried out. At the end of the refinement the R-factor was 12.3% and R' was 0.0259. A

shift factor of 0.8 was used throughout the refinement except in the last three cycles of anisotropic refinement when a value of 0.5 was applied. After the last cycle of refinement, the average parameter shift was 0.1σ and the largest shift was 0.67σ.

A summary of the least-squares refinement is shown below ($R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = \Sigma w\Delta^2/\Sigma wF_o^2$) :

Cycle No.	R	R'	No. of reflexions	Parameters refined
1	0.277		2620	
2	0.233		"	
3	0.208		"	
4	0.203		"	x,y,z, U_{iso}
5	0.201		"	for Br, O, C
6†	0.200		"	+ layer-scale
7	0.195		"	factors
8	0.179		"	
9	0.178		"	
10	0.178		"	
11	0.211	0.0760	3115	
12	0.156	0.0442	"	x,y,z, U_{ij}
13	0.129	0.0271	"	(i,j = 1,2,3)
14*	0.124	0.0261	"	for Br, O, C
15	0.123	0.0252	"	+ layer-scale
16*	0.122	0.0268	"	factors
17	0.123	0.0263	"	
18	0.123	0.0260	"	
19	0.123	0.0259	"	(structure factors only)

†Errors in $|F_o|$ for three reflexions were corrected.

*Adjustments in the parameters of the weighting scheme were made.

The weighting scheme used during the refinement was: $w = (p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{-1}$. The p-parameters were adjusted during the refinement. At the end of the refinement their final values ($p_1 = 1.20$, $p_2 = 0.0159$, $p_3 = 0.000632$) gave the following agreement analysis of averaged $w\Delta^2$ as a function of $|F_o|$ and of $\sin\theta/\lambda$:

$\|F_o\|$	$\langle w\Delta^2 \rangle$	No. of reflexions	$\sin\theta/\lambda$	$\langle w\Delta^2 \rangle$	No. of reflexions
0- 8	0.139	1811	0.0-0.2	0.302	136
8- 15	0.137	639	0.2-0.4	0.212	773
15- 31	0.208	413	0.4-0.6	0.130	1785
31- 61	0.239	197	0.6-0.8	0.115	420
61-122	0.222	49			
122-	0.219	5			

The analysis shows that the weighting scheme employed is a reasonable one, even though there is a somewhat greater variation of $\langle w\Delta^2 \rangle$ as a function of $\sin\theta/\lambda$ than of $|F_o|$.

The atomic scattering factors used throughout the analysis were taken from International Tables for X-Ray Crystallography (1962).

The final coordinates and thermal parameters are listed in Tables 4.1 and 4.2. The e.s.d.'s were derived from the inverse of the least-squares matrix. Observed and calculated structure factors are given in Table 4.3.

There are some discrepancies between $|F_o|$'s derived from the a-axis mounting and those from the b-axis mounting. They are most likely due to differences in spot shapes in the two sets of data. In order to evaluate the e.s.d.'s obtained from least-squares calculations, the approximate formula of Cruickshank (1960) ($\sigma(x) \sim R/\bar{s}(N/4p)^{\frac{1}{2}}$) was used to calculate mean coordinate standard deviations. The results of these calculations indicate that the e.s.d.'s should be increased by about 50%. Such an increase can also be justified in view of the fact that the block-diagonal approximation of the least-squares method was used and that corrections for absorption and for thermal vibration were neglected.

TABLE 4.1

FRACTIONAL COORDINATES AND E.S.D.s

ATOM	x/a	y/b	z/c
C(1)	0.7233 ± 11	0.4713 ± 7	0.3281 ± 5
C(2)	0.6244 ± 13	0.4659 ± 8	0.2299 ± 6
C(3)	0.7112 ± 13	0.3760 ± 9	0.1774 ± 6
C(4)	0.6753 ± 13	0.2716 ± 9	0.2204 ± 6
C(5)	0.7617 ± 10	0.2756 ± 7	0.3246 ± 5
C(6)	0.7163 ± 14	0.1752 ± 8	0.3748 ± 6
C(7)	0.8364 ± 15	0.1741 ± 8	0.4671 ± 7
C(8)	0.7940 ± 12	0.2693 ± 8	0.5262 ± 6
C(9)	0.8009 ± 12	0.3733 ± 7	0.4738 ± 6
C(10)	0.6781 ± 10	0.3689 ± 7	0.3769 ± 5
C(11)	0.7209 ± 17	0.4629 ± 9	0.5309 ± 6
C(12)	0.7959 ± 14	0.4485 ± 8	0.6287 ± 6
C(13)	0.8921 ± 13	0.3683 ± 8	0.6667 ± 5
C(14)	0.9457 ± 12	0.2721 ± 7	0.6134 ± 5
C(15)	0.9417 ± 15	0.3950 ± 10	0.7609 ± 6
C(16)	0.8656 ± 17	0.4871 ± 10	0.7697 ± 7
C(17)	1.1675 ± 11	0.2698 ± 10	0.5965 ± 6
C(18)	0.8039 ± 22	0.1923 ± 11	0.1702 ± 8
C(19)	0.4499 ± 15	0.2387 ± 11	0.2044 ± 6
C(20)	0.4467 ± 10	0.3642 ± 10	0.3882 ± 5

C(21)	0.5665 ± 13	0.6414 ± 8	0.1910 ± 5
C(22)	0.6343 ± 13	0.7281 ± 8	0.1319 ± 6
C(23)	0.7885 ± 14	0.7178 ± 9	0.0738 ± 6
C(24)	0.8357 ± 17	0.7980 ± 9	0.0192 ± 6
C(25)	0.7304 ± 15	0.8894 ± 9	0.0260 ± 6
C(26)	0.5899 ± 16	0.9044 ± 10	0.0845 ± 7
C(27)	0.5288 ± 17	0.8208 ± 9	0.1367 ± 8
O(1)	0.9397 ± 8	0.4853 ± 5	0.3294 ± 4
O(2)	0.6822 ± 9	0.5586 ± 6	0.1809 ± 4
O(3)	0.9810 ± 9	0.2827 ± 6	0.3256 ± 4
O(4)	0.9125 ± 9	0.1823 ± 6	0.6682 ± 4
O(5)	0.7717 ± 11	0.5252 ± 6	0.6885 ± 4
O(6)	0.4379 ± 11	0.6475 ± 7	0.2384 ± 5
Br(1)	0.8105 ± 2	1.0000 ± 0	-0.0478 ± 1

TABLE 4.2

ANISOTROPIC TEMPERATURE PARAMETERS AND E.S.D.s (A^{o2})

ATOM	U 11	U 22	U 33	2U 23	2U 31	2U 12
C(1)	0.0404 33	0.0355 37	0.0674 39	0.0165 65	0.0190 57	-0.0014 68
C(2)	0.0504 39	0.0399 40	0.0773 45	0.0139 77	0.0391 68	0.0010 82
C(3)	0.0533 41	0.0535 51	0.0697 43	0.0019 89	0.0273 69	-0.0039 96
C(4)	0.0572 46	0.0481 48	0.0694 43	0.0017 84	0.0157 71	-0.0202 94
C(5)	0.0363 32	0.0433 40	0.0618 36	0.0090 70	0.0210 56	-0.0043 75
C(6)	0.0679 54	0.0433 46	0.0727 46	-0.0050 86	-0.0080 79	-0.0169 95
C(7)	0.0704 56	0.0350 44	0.0800 49	0.0197 83	0.0050 86	0.0033 88
C(8)	0.0492 39	0.0423 41	0.0670 41	0.0134 76	0.0096 64	0.0012 81
C(9)	0.0496 39	0.0336 38	0.0700 39	0.0206 75	0.0032 62	0.0076 74
C(10)	0.0361 29	0.0356 35	0.0589 33	0.0162 63	0.0107 50	-0.0010 66
C(11)	0.0921 67	0.0387 42	0.0703 45	0.0050 82	-0.0437 86	0.0272 106
C(12)	0.0669 53	0.0438 46	0.0700 45	0.0101 84	0.0057 76	0.0126 97
C(13)	0.0525 40	0.0521 50	0.0603 38	0.0172 81	-0.0002 62	-0.0030 93

C(14)	0.0445	0.0411	0.0648	0.0296	0.0265	0.0062
	37	39	38	74	61	78
C(15)	0.0621	0.0640	0.0717	0.0114	0.0192	0.0030
	48	62	46	101	74	111
C(16)	0.0778	0.0533	0.0805	0.0011	0.0225	-0.0045
	59	58	52	105	87	117
C(17)	0.0339	0.0750	0.0664	0.0194	0.0075	0.0095
	31	65	41	99	58	100
C(18)	0.1114	0.0605	0.0798	-0.0155	0.0279	0.0232
	88	67	60	115	113	156
C(19)	0.0627	0.0794	0.0714	0.0044	0.0070	-0.0765
	53	76	49	109	80	125
C(20)	0.0347	0.0728	0.0548	0.0235	0.0035	-0.0079
	30	61	33	87	52	96
C(21)	0.0536	0.0441	0.0609	0.0015	-0.0074	0.0071
	43	44	40	72	66	83
C(22)	0.0575	0.0404	0.0641	0.0038	-0.0007	0.0080
	44	40	41	75	67	87
C(23)	0.0621	0.0585	0.0670	0.0149	0.0445	0.0187
	48	57	45	90	77	108
C(24)	0.0880	0.0492	0.0566	0.0050	0.0054	0.0032
	63	50	39	80	77	112
C(25)	0.0733	0.0500	0.0579	0.0204	-0.0180	-0.0179
	52	50	37	85	70	102
C(26)	0.0628	0.0565	0.0921	0.0036	0.0112	0.0233
	50	58	62	110	87	111
C(27)	0.0764	0.0515	0.0887	0.0152	0.0259	0.0439
	63	56	61	105	98	115
O(1)	0.0416	0.0395	0.0879	0.0256	0.0080	-0.0234
	25	32	35	63	46	54
O(2)	0.0528	0.0452	0.0702	0.0257	0.0124	0.0064
	28	33	31	58	48	61

O(3)	0.0438 26	0.0476 34	0.0844 36	0.0048 67	0.0216 49	0.0101 65
O(4)	0.0575 32	0.0517 37	0.0725 33	0.0418 65	0.0273 52	0.0316 69
O(5)	0.0729 36	0.0593 44	0.0667 30	-0.0073 68	0.0043 52	0.0004 81
O(6)	0.0685 36	0.0615 44	0.0789 36	0.0160 76	0.0592 60	0.0193 82
Br(1)	0.1000 8	0.0633 7	0.0875 6	0.0363 12	0.0116 11	-0.0275 14

TABLE 4.3

OBSERVED AND CALCULATED STRUCTURE FACTORS

DATA COLLECTED FROM THE a-AXIS MOUNTING

H	K	L	Fo²	σ(Fo²)

DATA COLLECTED FROM THE ω-AXIS SCANNING

H	K	L	F_o^2	$\sigma(F_o^2)$

DATA COLLECTED FROM THE b-AXIS MOUNTING

H	K	L	|Fo|	|Fc|
0	0	2	20.9	17.3
0	0	4	56.5	57.8
0	0	6	0.5	0.9
0	0	8	30.8	28.9
0	0	10	23.7	24.8
0	0	12	55.8	39.2
0	0	14	73.1	58.1
0	0	16	34.8	27.4
0	0	18	6.0	5.7
0	0	20	21.5	17.7
0	0	22	30.2	25.6
0	0	24	9.2	7.6
0	0	26	6.5	5.1
0	0	28	20.0	17.0
0	0	30	4.7	3.5
0	0	32	0.0	1.3
0	0	34	0.8	0.4
0	0	36	1.8	1.2
0	0	38	5.1	3.5
0	0	40	8.9	8.3
0	0	42	4.9	4.1
0	0	44	14.4	12.7
0	0	46	15.2	13.2
0	0	48	7.5	6.8
0	0	50	18.3	14.6
0	0	52	0.0	0.7
0	0	54	21.7	16.1
0	0	56	15.6	10.8
0	0	58	3.7	3.4
0	0	60	45.6	36.8
0	0	62	29.1	23.1
0	0	64	70.2	63.4
0	0	66	88.9	93.7
0	0	68	18.9	20.7
0	0	70	58.3	71.1
0	0	72	23.5	31.2
0	0	74	4.1	7.4
0	0	76	36.6	41.4
0	0	78	75.7	72.0
0	0	80	60.4	71.3
0	0	82	78.0	74.7
0	0	84	19.3	8.3
0	0	86	15.2	16.5
0	0	88	25.6	23.0
0	0	90	10.1	11.1
0	0	92	18.1	17.8
0	0	94	7.2	7.8
0	0	96	16.6	17.3
0	0	98	10.8	8.6
0	0	100	1.1	1.3
0	0	102	6.7	6.9
0	0	104	3.6	3.5
0	0	106	7.4	7.4
0	0	108	1.6	0.7
0	0	110	1.1	1.3
0	0	112	1.2	1.2
0	0	114	2.1	2.1
0	0	116	1.2	1.2
0	0	118	1.2	1.2
0	0	120	1.2	1.2
0	0

6. Absolute configuration

The absolute configuration was determined by the anomalous dispersion method (Bijvoet, 1955) from an hkl precession photograph, taken with Mo Kα radiation, which was indexed with respect to a right-handed set of axes (Peerdeman and Bijvoet, 1956). With Mo Kα radiation the value of $\Delta f''$ for bromine is 2.6 at $\sin\theta = 0$. The intensities of 17 Bijvoet pairs of reflexions which appeared different were measured visually and used in this determination. The observed intensities, calculated structure factors, and the ratios $I_o(hk\ell)/I_o(\bar{h}\bar{k}\bar{\ell})$ and $F_c^2(hk\ell)/F_c^2(\bar{h}\bar{k}\bar{\ell})$ for these pairs can be seen in Table 4.4. For each pair the ratios of intensities and of F_c^2 are either both smaller than 1 or both greater than 1, except for two pairs (1,11,1 and 2,7,1) where the ratios of F_c^2 are approximately 1. There is therefore no doubt about the correctness of the absolute configuration.

All the listed coordinates, anisotropic thermal parameters, and the diagrams refer to a molecule with the correct absolute configuration relative to a right-handed set of axes. Orthogonal coordinates (in Å) are listed in Table 4.5 and principal values of the vibration tensors in Table 4.6.

TABLE 4.4

SOME RELATIONSHIPS OF THE BIJVOET PAIRS USED TO DETERMINE THE ABSOLUTE CONFIGURATION

h	k	ℓ	$I_o(hk\ell)$*	$I_o(\bar{h}\bar{k}\bar{\ell})$*	$F_c(hk\ell)$	$F_c(\bar{h}\bar{k}\bar{\ell})$	$\frac{I_o(hk\ell)}{I_o(\bar{h}\bar{k}\bar{\ell})}$	$\frac{F_c^2(hk\ell)}{F_c^2(\bar{h}\bar{k}\bar{\ell})}$
1	5	$\bar{1}$	2.0	4.0	8.9	14.9	0.50	0.36
1	7	1	11.0	13.0	23.0	26.3	0.85	0.76
1	11	1	5.5	8.0	20.0	20.2	0.69	0.98
2	2	$\bar{1}$	11.0	7.0	20.8	16.8	1.57	1.53
2	3	1	15.0	13.0	27.6	25.2	1.15	1.17
2	5	$\bar{1}$	28.0	24.0	37.7	32.3	1.17	1.36
2	6	$\bar{1}$	4.0	2.5	12.3	11.7	1.60	1.11
2	6	1	22.0	18.0	31.4	27.5	1.22	1.30
2	7	$\bar{1}$	2.0	4.0	12.8	16.2	0.50	0.62
2	7	1	5.0	6.0	19.9	19.8	0.83	1.01
2	10	1	5.0	6.0	18.3	19.3	0.83	0.90
3	1	1	7.0	5.5	17.3	13.1	1.27	1.74
3	3	1	5.0	7.0	15.1	17.3	0.71	0.76
3	4	1	2.0	3.0	12.8	14.6	0.67	0.77
3	10	1	2.0	4.0	15.0	16.1	0.50	0.87
4	1	1	10.0	9.0	27.7	25.0	1.11	1.23
4	5	1	4.5	3.5	17.2	16.0	1.29	1.16

*The intensities are on an arbitrary scale.

TABLE 4.5

ORTHOGONAL COORDINATES IN ANGSTRØM AND E.S.D.s

ATOM	X'	Y	Z'
C(1)	4.732 ± 8	6.127 ± 9	4.487 ± 8
C(2)	4.085 ± 9	6.057 ± 10	3.083 ± 9
C(3)	4.653 ± 8	4.887 ± 11	2.261 ± 8
C(4)	4.419 ± 9	3.530 ± 11	2.916 ± 9
C(5)	4.983 ± 7	3.582 ± 10	4.415 ± 7
C(6)	4.687 ± 9	2.277 ± 11	5.182 ± 10
C(7)	5.472 ± 10	2.263 ± 11	6.487 ± 10
C(8)	5.195 ± 8	3.501 ± 10	7.383 ± 8
C(9)	5.240 ± 8	4.852 ± 9	6.605 ± 9
C(10)	4.436 ± 7	4.795 ± 9	5.233 ± 7
C(11)	4.717 ± 11	6.017 ± 11	7.490 ± 10
C(12)	5.208 ± 9	5.830 ± 11	8.901 ± 9
C(13)	5.837 ± 8	4.788 ± 11	9.413 ± 8
C(14)	6.187 ± 8	3.538 ± 9	8.597 ± 8
C(15)	6.161 ± 10	5.134 ± 14	10.783 ± 10
C(16)	5.663 ± 11	6.332 ± 14	10.954 ± 10
C(17)	7.639 ± 7	3.506 ± 13	8.233 ± 8
C(18)	5.260 ± 15	2.499 ± 14	2.107 ± 11
C(19)	2.944 ± 10	3.103 ± 15	2.796 ± 9
C(20)	2.922 ± 7	4.734 ± 12	5.519 ± 7

C(21)	3.707 ± 8	8.338 ± 10	2.537 ± 8
C(22)	4.150 ± 9	9.464 ± 10	1.626 ± 9
C(23)	5.159 ± 9	9.330 ± 12	0.687 ± 8
C(24)	5.468 ± 11	10.373 ± 11	-0.146 ± 9
C(25)	4.779 ± 10	11.561 ± 11	0.009 ± 9
C(26)	3.859 ± 10	11.756 ± 13	0.948 ± 11
C(27)	3.460 ± 11	10.670 ± 12	1.752 ± 11
O(1)	6.148 ± 5	6.308 ± 7	4.395 ± 6
O(2)	4.464 ± 6	7.261 ± 7	2.327 ± 6
O(3)	6.418 ± 6	3.674 ± 8	4.316 ± 6
O(4)	5.970 ± 6	2.370 ± 8	9.426 ± 6
O(5)	5.049 ± 7	6.827 ± 8	9.799 ± 6
O(6)	2.865 ± 7	8.416 ± 9	3.304 ± 7
Br(1)	5.303 ± 1	12.999 ± 0	-1.125 ± 1

TABLE 4.6

PRINCIPAL VALUES OF VIBRATION TENSORS AND THEIR DIRECTION COSINES REFERRED TO ORTHOGONAL AXES

ATOM	$U(A^{o2})$	D1	D2	D3
C(1)	0.0699	0.1999	0.2269	0.9532
	0.0327	-0.3135	-0.9069	0.2816
	0.0399	0.9283	-0.3551	-0.1102
C(2)	0.0836	0.4238	0.1468	0.8938
	0.0377	-0.3454	-0.8860	0.3093
	0.0441	0.8373	-0.4398	-0.3248
C(3)	0.0729	0.4353	0.0076	0.9003
	0.0478	-0.8364	-0.3664	0.4075
	0.0544	0.3330	-0.9304	-0.1532
C(4)	0.0412	-0.5475	-0.8288	0.1158
	0.0699	0.3080	-0.0709	0.9488
	0.0631	-0.7781	0.5551	0.2941
C(5)	0.0637	0.2506	0.1912	0.9490
	0.0329	-0.8970	-0.3227	0.3020
	0.0437	0.3640	-0.9270	0.0907
C(6)	0.0400	0.3303	0.9333	0.1408
	0.0813	-0.6117	0.0980	0.7850
	0.0641	0.7189	-0.3454	0.6033
C(7)	0.0329	0.0594	-0.9772	0.2037
	0.0831	-0.2052	0.1877	0.9606
	0.0700	-0.9769	-0.0989	-0.1893
C(8)	0.0687	0.0543	0.2458	0.9678
	0.0406	0.0409	-0.9690	0.2438
	0.0492	0.9977	0.0263	-0.0627
C(9)	0.0731	-0.0558	0.2407	0.9690
	0.0301	0.2135	-0.9452	0.2471
	0.0505	0.0000	0.0000	0.0000
C(10)	0.0614	0.0888	0.2985	0.9503
	0.0325	-0.3450	-0.8858	0.3105
	0.0364	0.9344	-0.3554	0.0243

C(11)	0.1152	-0.8062	-0.1325	0.5767
	0.0331	0.3411	-0.9004	0.2700
	0.0572	0.4835	0.4144	0.7711
C(12)	0.0413	0.2508	-0.9529	0.1705
	0.0717	-0.3756	0.0666	0.9244
	0.0681	-0.8922	-0.2959	-0.3413
C(13)	0.0676	-0.2792	0.4910	0.8252
	0.0466	0.1846	-0.8159	0.5479
	0.0514	0.9423	0.3053	0.1371
C(14)	0.0741	0.3249	0.4081	0.8532
	0.0336	-0.1882	-0.8562	0.4812
	0.0413	0.9268	-0.3169	-0.2014
C(15)	0.0759	0.3355	0.4369	0.8346
	0.0597	-0.7553	-0.4047	0.5155
	0.0616	0.5629	-0.8034	0.1942
C(16)	0.0530	-0.1000	-0.9939	0.0465
	0.0840	0.6441	-0.0290	0.7644
	0.0737	-0.7583	0.1064	0.6431
C(17)	0.0334	0.0000	0.0000	0.0000
	0.0814	0.0963	0.8417	0.5313
	0.0605	-0.0594	-0.5280	0.8472
C(18)	0.1142	0.9761	0.1952	0.0960
	0.0542	-0.2170	0.9050	0.3660
	0.0822	-0.0155	-0.3781	0.9256
C(19)	0.1108	-0.6195	0.7748	0.1258
	0.0318	-0.7755	-0.6289	0.0546
	0.0712	0.1214	-0.0637	0.9906
C(20)	0.0793	-0.0886	0.8896	0.4481
	0.0343	-0.9942	-0.1069	0.0155
	0.0490	0.0617	-0.4441	0.8939
C(21)	0.0670	-0.5205	-0.0631	0.8516
	0.0424	0.4129	-0.8915	0.1863
	0.0505	0.7474	0.4486	0.4900
C(22)	0.0392	0.2395	-0.9652	0.1053
	0.0673	-0.4488	-0.0139	0.8935
	0.0562	-0.8610	-0.2612	-0.4365

C(23)	0.0854	0.6463	0.3887	0.6567
	0.0452	-0.7573	0.2217	0.6142
	0.0542	0.0931	-0.8943	0.4376
C(24)	0.0886	-0.9910	-0.0324	0.1301
	0.0483	0.0697	-0.9532	0.2941
	0.0573	0.1145	0.3005	0.9469
C(25)	0.0878	-0.7668	0.3394	0.5448
	0.0430	0.0236	-0.8333	0.5524
	0.0527	0.6414	0.4364	0.6309
C(26)	0.0476	0.6076	-0.7942	0.0066
	0.0922	0.0376	0.0371	0.9986
	0.0717	-0.7933	-0.6065	0.0524
C(27)	0.0387	0.4979	-0.8666	0.0334
	0.0975	0.6260	0.3858	0.6777
	0.0794	-0.6002	-0.3165	0.7346
O(1)	0.0918	-0.0474	0.2640	0.9634
	0.0269	-0.6169	-0.7662	0.1797
	0.0505	0.7856	-0.5858	0.1992
O(2)	0.0757	0.1365	0.3911	0.9101
	0.0395	0.1634	-0.9151	0.3687
	0.0527	0.9771	0.0984	-0.1888
O(3)	0.0850	0.1849	0.0775	0.9797
	0.0397	-0.8498	0.5133	0.1198
	0.0501	-0.4936	-0.8547	0.1608
O(4)	0.0914	0.4433	0.5339	0.7200
	0.0351	0.4453	-0.8283	0.3400
	0.0538	0.7779	0.1699	-0.6050
O(5)	0.0578	0.0795	0.9186	0.3872
	0.0749	-0.8744	-0.1223	0.4695
	0.0668	0.4787	-0.3759	0.7935
O(6)	0.1000	0.6388	0.2944	0.7108
	0.0468	-0.7687	0.2047	0.6060
	0.0584	0.0329	-0.9335	0.3570
Br(1)	0.0502	-0.2227	-0.8722	0.4355
	0.1089	-0.7723	0.4305	0.4673
	0.0920	-0.5950	-0.2322	-0.7694

7. Description and discussion of the structure

This analysis establishes the structure and absolute configuration of the p-bromobenzoate derivative of ε-caesalpin to be VI and hence that of ε-caesalpin to be VII. The stereochemistry and conformation of the structure can be seen clearly from Figures 4.2 and 4.3. The *trans*-fused rings A and B both occur in the chair conformation while the unsaturated ring C adopts a distorted half-chair form. Rings B and C are also *trans*-fused.

Bond lengths, valency angles, and their e.s.d.'s are listed in Table 4.7; the structure (including bond lengths and angles) is shown in Figure 4.4. The least-squares planes are listed in Table 4.8. In this discussion an increase of 50% in the e.s.d.'s listed in the tables will be assumed for reasons outlined above. Deviations from normal values of bond lengths and angles are considered genuine at a 0.1% significance level. There are several such deviations; most of them can be attributed to strain arising from repulsive forces.

The only four atoms in ring A which lie in a plane are C(2), C(3), C(5), and C(10). Atoms C(1) and C(4) are displaced from this plane by +0.725 and -0.668 Å, respectively. In a cyclohexane chair with all angles tetrahedral this displacement is equal to 0.73 Å. Since carbon atom

Figure 4.2

View of the molecule along the a axis.

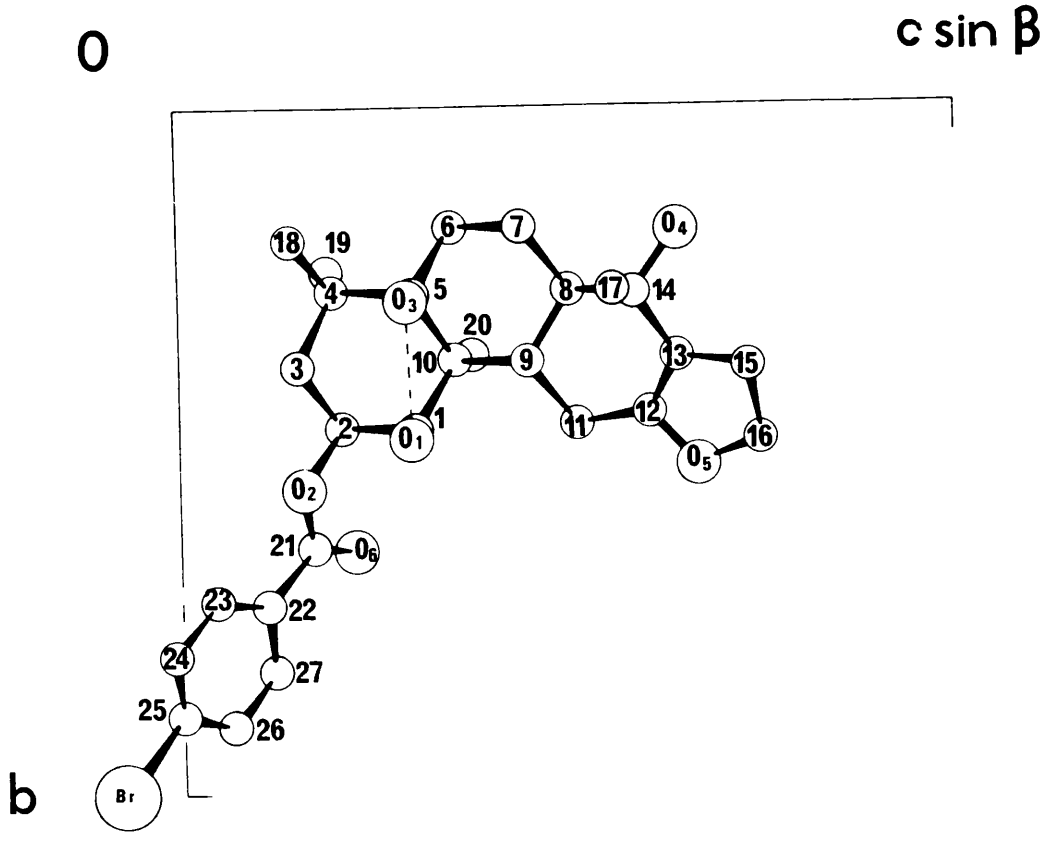

0
c sin β
b
18
19
6
7
O4
4
O3
5
8
17
14
20
3
10
9
13
15
2
O1
1
11
12
16
O5
O2
21
O6
23
22
24
27
25
26
Br

Figure 4.3

View of the molecule along the b-axis.

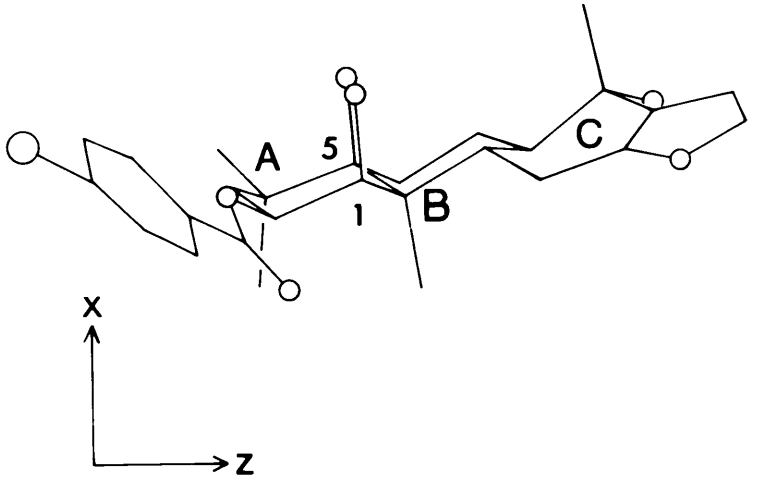

A
5
1
B
C
X
Z

TABLE 4.7

MOLECULAR DIMENSIONS

(a) Bond lengths and e.s.d.'s

C(1) -C(2)	1.547 ± 12 Å	C(2) -O(2)	1.472 ± 12 Å
C(2) -C(3)	1.539 ± 14		
C(3) -C(4)	1.525 ± 15	C(13)-C(15)	1.450 ± 13
C(4) -C(5)	1.603 ± 11	C(12)-C(13)	1.321 ± 14
C(4) -C(18)	1.558 ± 17	C(15)-C(16)	1.308 ± 19
C(4) -C(19)	1.540 ± 14	C(12)-O(5)	1.351 ± 13
C(5) -C(6)	1.542 ± 14	C(16)-O(5)	1.398 ± 13
C(5) -C(10)	1.562 ± 12		
C(6) -C(7)	1.524 ± 14	C(21)-O(2)	1.333 ± 12
C(7) -C(8)	1.553 ± 14	C(21)-O(6)	1.142 ± 11
C(8) -C(9)	1.560 ± 13		
C(8) -C(14)	1.568 ± 11	C(21)-C(22)	1.515 ± 13
C(9) -C(10)	1.591 ± 11		
C(9) -C(11)	1.555 ± 14	C(22)-C(23)	1.385 ± 12
C(10)-C(20)	1.542 ± 10	C(23)-C(24)	1.370 ± 15
C(14)-C(17)	1.497 ± 11	C(24)-C(25)	1.382 ± 16
		C(25)-C(26)	1.329 ± 14
C(11)-C(12)	1.505 ± 14	C(26)-C(27)	1.409 ± 17
C(13)-C(14)	1.534 ± 13	C(27)-C(22)	1.395 ± 15
C(1) -O(1)	1.430 ± 9	C(25)-Br	1.905 ± 10
C(5) -O(3)	1.441 ± 9		
C(14)-O(4)	1.448 ± 12		

(b) Bond angles and e.s.d.'s

C(2) -C(1) -C(10)	108.5 ± 0.7°	C(8) -C(14)-C(13)	106.7 ± 0.7°
C(2) -C(1) -O(1)	111.2 ± 0.6	C(8) -C(14)-C(17)	115.2 ± 0.7
C(10)-C(1) -O(1)	109.1 ± 0.6	C(8) -C(14)-O(4)	109.2 ± 0.7
C(1) -C(2) -C(3)	111.4 ± 0.7	C(13)-C(14)-C(17)	111.6 ± 0.8
C(1) -C(2) -O(2)	108.8 ± 0.7	C(13)-C(14)-O(4)	108.5 ± 0.7
C(3) -C(2) -O(2)	104.6 ± 0.7	C(17)-C(14)-O(4)	105.5 ± 0.7
C(2) -C(3) -C(4)	112.9 ± 0.7		
C(3) -C(4) -C(5)	108.6 ± 0.8	C(11)-C(12)-C(13)	128.1 ± 0.9
C(3) -C(4) -C(18)	106.4 ± 0.8	C(11)-C(12)-O(5)	119.5 ± 0.9
C(3) -C(4) -C(19)	111.1 ± 0.8	C(12)-C(13)-C(14)	123.1 ± 0.8
C(5) -C(4) -C(18)	108.5 ± 0.8	C(14)-C(13)-C(15)	130.3 ± 0.9
C(5) -C(4) -C(19)	114.8 ± 0.7		
C(18)-C(4) -C(19)	107.0 ± 0.9	C(12)-O(5) -C(16)	103.7 ± 0.9
C(4) -C(5) -C(6)	111.7 ± 0.8	C(12)-C(13)-C(15)	106.5 ± 0.9
C(4) -C(5) -C(10)	113.1 ± 0.7	C(13)-C(15)-C(16)	104.9 ± 0.9
C(4) -C(5) -O(3)	106.8 ± 0.6	C(15)-C(16)-O(5)	112.6 ± 1.0
C(6) -C(5) -C(10)	109.2 ± 0.6	C(13)-C(12)-O(5)	112.3 ± 0.8
C(6) -C(5) -O(3)	106.3 ± 0.7		
C(10)-C(5) -O(3)	109.6 ± 0.7	C(2) -O(2) -C(21)	115.8 ± 0.7
C(5) -C(6) -C(7)	109.6 ± 0.8		
C(6) -C(7) -C(8)	113.3 ± 0.8	C(22)-C(21)-O(2)	109.9 ± 0.7
C(7) -C(8) -C(9)	113.4 ± 0.7	C(22)-C(21)-O(6)	124.7 ± 1.0
C(7) -C(8) -C(14)	110.6 ± 0.7	O(2) -C(21)-O(6)	125.4 ± 1.0
C(9) -C(8) -C(14)	110.4 ± 0.7		
C(8) -C(9) -C(10)	112.6 ± 0.7	C(21)-C(22)-C(23)	123.3 ± 0.9
C(8) -C(9) -C(11)	110.8 ± 0.7	C(21)-C(22)-C(27)	116.3 ± 0.8
C(10)-C(9) -C(11)	110.4 ± 0.7	C(23)-C(22)-C(27)	120.3 ± 1.0
C(1) -C(10)-C(5)	110.3 ± 0.6	C(22)-C(23)-C(24)	120.2 ± 1.0
C(1) -C(10)-C(9)	106.7 ± 0.6	C(23)-C(24)-C(25)	118.3 ± 0.9
C(1) -C(10)-C(20)	108.1 ± 0.7	C(24)-C(25)-C(26)	123.4 ± 1.0
C(5) -C(10)-C(9)	107.6 ± 0.6	C(24)-C(25)-Br	116.4 ± 0.7
C(5) -C(10)-C(20)	114.2 ± 0.7	C(26)-C(25)-Br	120.1 ± 0.9
C(9) -C(10)-C(20)	109.7 ± 0.6	C(25)-C(26)-C(27)	119.1 ± 1.1
C(9) -C(11)-C(12)	109.3 ± 0.9	C(22)-C(27)-C(26)	118.3 ± 1.0

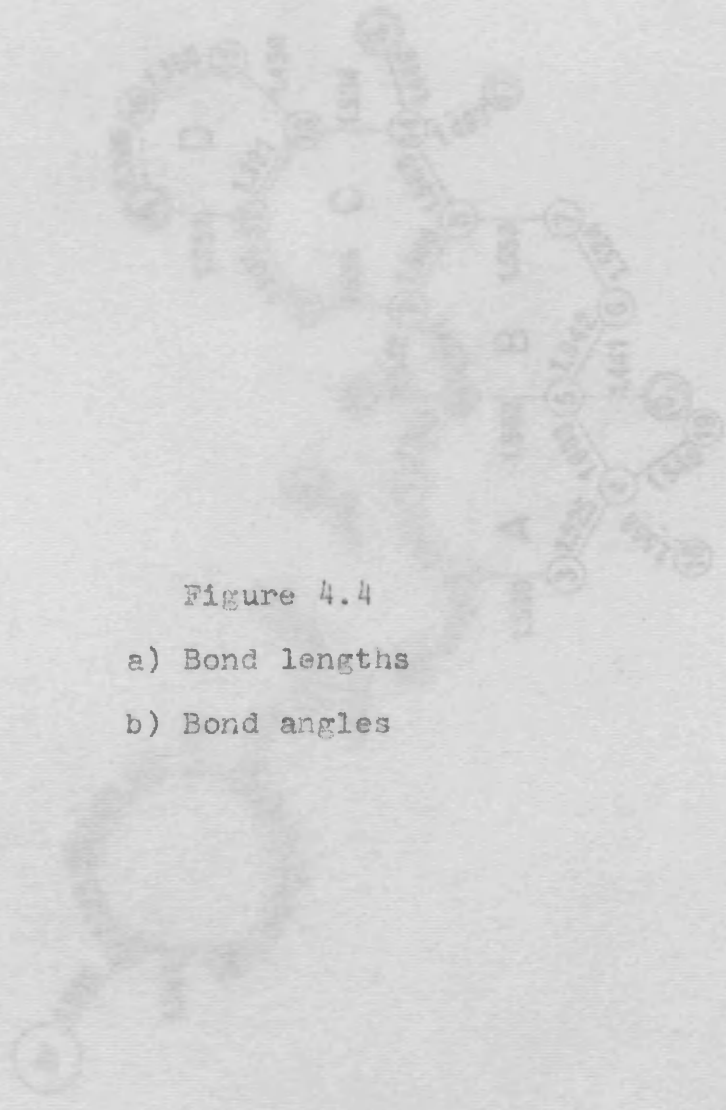
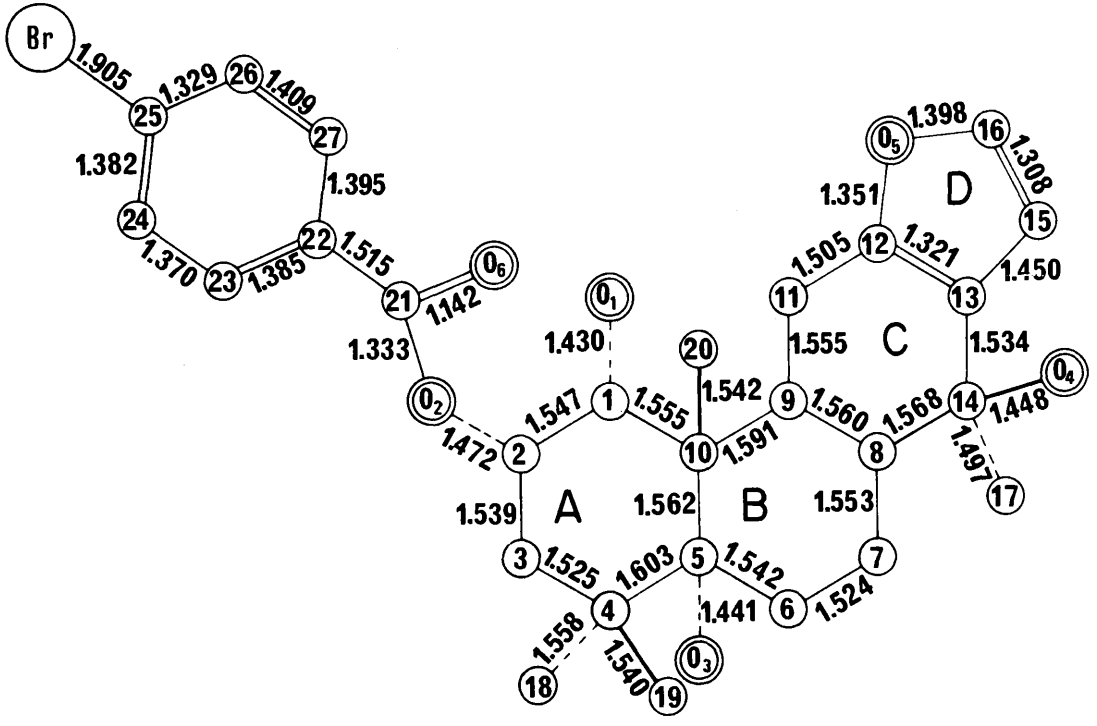


Figure 4.4

a) Bond lengths

b) Bond angles


Br
1.905
1.329
26
1.409
25
27
1.382
1.395
24
22
1.515
1.370
23
1.385
21
1.142
O_6
1.333
O_2
1.472
2
1.547
1
1.555
O_1
1.430
20
1.542
10
1.591
9
1.560
1.568
14
1.448
O_4
1.497
17
8
1.553
7
1.524
6
1.441
O_3
1.539
A
1.562
B
3
1.525
1.603
5
1.542
4
1.558
1.540
18
19
1.555
C
1.534
11
12
1.321
13
1.450
1.505
1.351
O_5
1.398
16
1.308
15
D

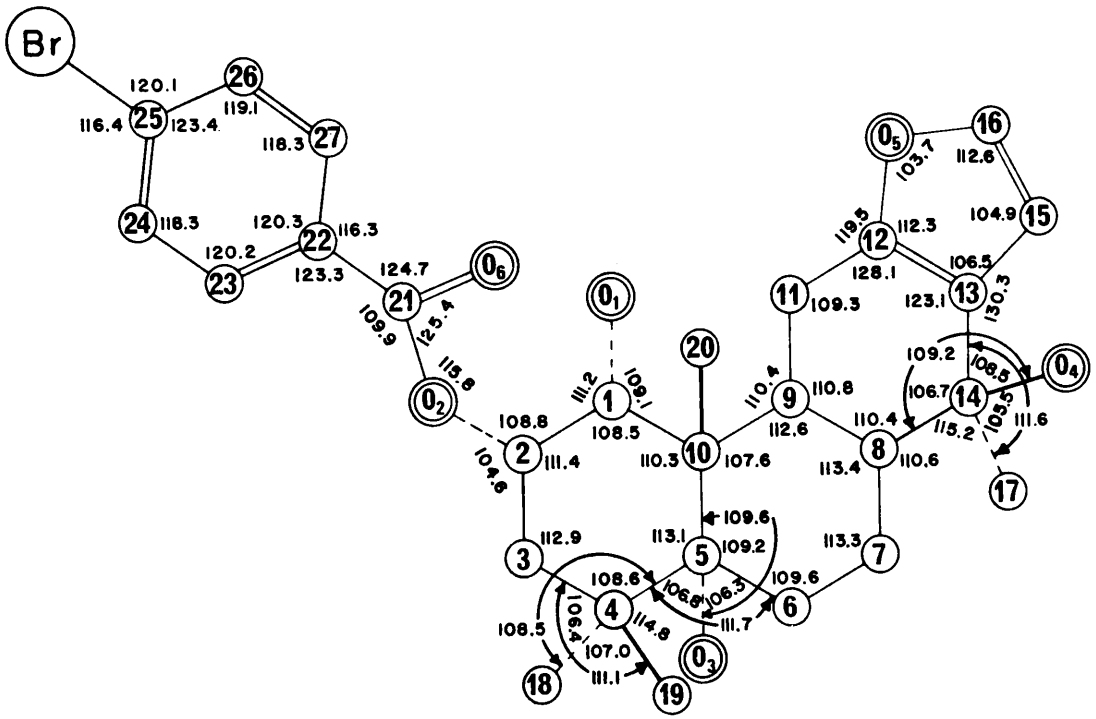

Br
120.1
26
116.4
25
123.4
119.1
27
118.3
24
118.3
120.3
22
116.3
120.2
23
123.3
124.7
21
O_6
109.9
125.4
115.8
O_2
O_1
111.2
109.1
1
20
108.8
108.5
2
111.4
110.3
10
107.6
104.6
3
112.9
113.1
5
109.2
109.6
108.6
106.8
106.3
4
114.8
111.7
6
109.6
108.5
109.4
107.0
111.1
18
19
O_3
O_5
103.7
16
112.6
104.9
15
119.5
12
112.3
128.1
106.5
11
109.3
123.1
13
130.3
109.2
108.8
O_4
106.7
14
105.5
115.2
111.6
17
110.4
9
110.8
112.6
8
110.6
113.4
7
113.3

TABLE 4.8

LEAST-SQUARES PLANES

Plane 1
Ring A

Atom	Δ(Å)
C(2)	-0.009
C(3)	0.009
C(5)	-0.009
C(10)	0.009
C(1)*	0.725
C(4)*	-0.668

$\overline{\Delta^2}$ = 0.009
χ^2 = 4.54

Plane 2
Ring B

Atom	Δ(Å)
C(10)	-0.062
C(5)	0.065
C(7)	-0.066
C(8)	0.063
C(6)*	-0.719
C(9)*	0.629

$\overline{\Delta^2}$ = 0.064
χ^2 = 204.9

Plane 3
Ring C

Atom	Δ(Å)
C(11)	0.000
C(12)	0.001
C(13)	-0.001
C(14)	0.000
C(8)*	-0.582
C(9)*	0.205

$\overline{\Delta^2}$ = 0.001
χ^2 = 0.02

Plane 4
Ring D

Atom	Δ(Å)
C(12)	0.007
C(13)	-0.008
C(15)	0.007
C(16)	-0.004
O(5)	-0.002
C(11)*	0.069
C(14)*	0.043

$\overline{\Delta^2}$ = 0.006
χ^2 = 1.88

Plane 5
Ester Group

Atom	Δ(Å)
C(21)	-0.007
C(22)	0.002
O(2)	0.002
O(6)	0.003
C(2)*	-0.096

$\overline{\Delta^2}$ = 0.004
χ^2 = 0.91

Plane 6
Aromatic Ring

Atom	Δ(Å)
Br	-0.003
C(21)	-0.015
C(22)	0.010
C(23)	0.028
C(24)	-0.012
C(25)	-0.025
C(26)	0.036
C(27)	-0.019
O(2)*	0.041
O(6)*	-0.050
C(2)*	-0.067

$\overline{\Delta^2}$ = 0.021
χ^2 = 40.54

*Atoms not included in the calculation of the plane.

Plane	Equations for the least-squares planes
1	$0.923\ X' + 0.377\ Y + 0.079\ Z' = 6.307$ Å
2	$0.933\ X' + 0.355\ Y - 0.058\ Z' = 5.600$
3	$0.878\ X' + 0.409\ Y - 0.250\ Z' = 4.724$
4	$0.870\ X' + 0.395\ Y - 0.295\ Z' = 4.204$
5	$0.649\ X' + 0.313\ Y + 0.693\ Z' = 6.781$
6	$0.681\ X' + 0.296\ Y + 0.670\ Z' = 6.707$

(X', Y, Z' are orthogonal coordinates (in Å), i.e. $X' = X\sin\beta$ and $Z' = Z + X\cos\beta$).

C(4) is bent towards the ring-A plane by about 0.06 Å an increase in the adjacent angles from the tetrahedral value to about 111.5° is expected (Sim, 1965), assuming that all the bond lengths are normal and that the other angles are tetrahedral. The angles C(2)-C(3)-C(4) and C(4)-C(5)-C(10) were found to be 112.9 and 113.1°, respectively. These slight distortions in ring A are mainly due to the interaction between the two diaxial methyl carbon atoms C(19) and C(20). It can be seen that they are bent away from each other by comparing the C(4)...C(10) non-bonded distance (2.640 Å) with the much longer C(19)...C(20) distance (3.175 Å). The bending of the two diaxial methyl groups also causes significant increases from the normal value in the two angles C(5)-C(4)-C(19) (114.8°) and C(5)-C(10)-C(20) (114.2°). The distortions observed here are practically identical with those in the two previously described structures. In these three diterpenoids one angle at each carbon atom to which an axial methyl group is bonded has a value significantly larger than tetrahedral. The derivatives of taxadienetetraol and ε-caesalpin thus have two such increased angles since they contain two diaxial methyl groups, while p-bromophenacyl labdanolate has three increased angles. The non-bonded 1,3 C...C distances inside the rings and the non-bonded CH_3...CH_3

distances together with the increased angles are listed below. They are also compared with the corresponding distances in other compounds containing 1,3 diaxial methyl groups. The pattern of these distances is the same in all compounds. The mean value of the 1,3 C...C distances inside the rings is 2.648 Å and the distances between the axial methyl groups are much larger (mean value 3.196 Å).

Non-bonded 1,3 C...C dist. inside ring		Non-bonded $CH_3...CH_3$ dist.		Increased angle		Compound
C(4)...C(8)	2.60Å	C(16)...C(20)	3.16Å	C(3)-C(4) -C(16)	117.6°	a
				C(3)-C(8) -C(20)	117.4	
C(4)...C(10)	2.67	C(18)...C(20)	3.31	C(5)-C(4) -C(18)	114.9	
C(8)...C(10)	2.65	C(17)...C(20)	3.12	C(9)-C(8) -C(17)	116.1	b
				C(5)-C(10)-C(20)	114.7	
C(4)...C(10)	2.64	C(19)...C(20)	3.18	C(5)-C(4) -C(19)	114.8	c
				C(5)-C(10)-C(20)	114.2	
C(4)...C(10)	2.82	C(24)...C(25)	3.17	C(3)-C(4) -C(24)	115.3	
C(8)...C(10)	2.59	C(26)...C(25)	3.30	C(9)-C(8) -C(26)	113.8	d
				C(9)-C(10)-C(25)	115.8	
C(8)...C(10)	2.61	C(19)...C(30)	3.04	C(9)-C(8) -C(30)	117	e
C(4)...C(10)	2.70	C(19)...C(31)	3.29	C(5)-C(10)-C(19)	112.7	f
2.648Å		3.196Å		115.4°		mean values

a Taxadienetetraol derivative

b p-Bromophenacyl labdanolate

c ε-Caesalpin derivative

d Methyl melaleucate iodoacetate (Hall and Maslen, 1965)

e Cedrelone iodoacetate (Grant, Hamilton, Hamor, Robertson, and Sim, 1963)

f 3β-Acetoxy-7α, 11α-dibromolanostane-8α, 9α-epoxide (Fawcett and Trotter, 1966).

The two 1,3-diaxial bonds of the hydroxyl groups O(1) and O(3) are approximately parallel to each other, the non-bonded distance C(1)...C(5) (2.558 Å) being only slightly shorter than the O(1)...O(3) distance (2.649 Å). The latter distance represents an intramolecular hydrogen bond which will be discussed later.

A least-squares plane was calculated through the ring-B atoms C(10), C(5), C(7), and C(8). As can be seen from Table 4.8, these atoms are not coplanar. The "best" plane through them makes a dihedral angle of 8.0° with the ring-A plane instead of being parallel to it. The atoms C(9) and C(6) are displaced from this plane by +0.629 and -0.719 Å, respectively. The distortion of ring B can probably be attributed to strain caused by the junction to the unsaturated ring C. The angle C(7)-C(8)-C(9) (113.4°) is significantly larger than tetrahedral. It is also on the large side of the value 110.5°, obtained from theoretical calculations (Bucourt and Heinaut, 1965), even though not significantly so.

Ring C occurs, as mentioned earlier, in a distorted half-chair conformation. Atoms C(11), C(12), C(13), and C(14) are coplanar while C(9) and C(8) are displaced above and below this plane by 0.205 and 0.582 Å, respectively. According to calculations by Corey and Sneen (1955) these

displacements should be ±0.43 Å, and in pentachlorocyclohexene (Pasternak, 1951) the observed values were fairly similar, *viz.* 0.34 and 0.40 Å. On the basis of energy considerations Bucourt and Heinaut (1965) calculated that in a 4,5-disubstituted cyclohexene ring the angles at the trigonal carbon atoms should be 124.0° and at the other atoms in the ring 110.5°. The angle C(8)-C(14)-C(13) (106.7°) deviates significantly from 110.5° and the angle C(11)-C(12)-C(13) (128.1°) is larger than 124.0° even though the last deviation is not significant at a 0.1% level. A closing of the former angle brings C(8) further away from the ring-C plane and an opening of the latter angle decreases the distance of C(9) to the same plane. These deviations in angles are therefore a measure of the distortion in ring C. The hydroxyl group O(4) and the methyl group C(17) are, respectively, in the quasi-equatorial and quasi-axial positions. The methyl group is slightly bent towards the hydroxyl group giving rise to the significantly abnormal angles C(8)-C(14)-C(17) (115.2°) and C(17)-C(14)-O(4) (105.5°).

The furan ring is flat but its plane is slightly tilted with respect to the ring-C plane (the dihedral angle between the two planes is 2.7°). As can be seen from the comparisons listed below, all the bond lengths and angles in the

furan ring agree within experimental error with the values found in furan itself (Bak *et al*, 1962) and with the values in 3,4-furandicarboxylic acid (Williams and Rundle, 1964).

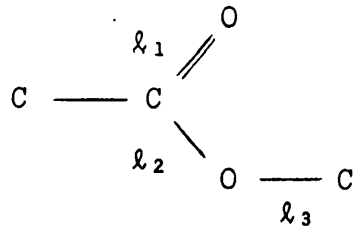
Furan ring in ε-caesalpin		3,4-Furandicarboxylic acid	Furan
C(12)-O(5)	1.351Å	1.361 ± 0.003Å	1.362 ± 0.001Å
C(16)-O(5)	1.398		
C(12)-C(13)	1.321	1.351 ± 0.003	1.361 ± 0.001
C(15)-C(16)	1.308		
C(13)-C(15)	1.450	1.462 ± 0.005	1.431 ± 0.002
C(12)-O(5) -C(16)	103.7°	107.2 ± 0.3°	106.6 ± 0.1°
C(13)-C(12)-O(5)	112.3	110.8 ± 0.2	110.7 ± 0.1
C(15)-C(16)-O(5)	112.6		
C(13)-C(15)-C(16)	104.9	105.6 ± 0.2	106.1 ± 0.1
C(12)-C(13)-C(15)	106.5		
C(12)-C(13)-C(14)	123.1	124.0 ± 0.2	
C(14)-C(13)-C(15)	130.3	130.3 ± 0.2	

It is remarkable that the three angles at carbon atom C(13) agree within 0.9° with the corresponding angles in 3,4-furandicarboxylic acid.

The entire p-bromobenzoate group is not planar, but the aromatic ring and the two atoms attached to it, bromine

and C(21), are in one plane. Atoms C(21), O(2), and O(6) of the ester group and atom C(22) are coplanar, but C(2) is displaced from this plane by 0.096 Å. The ester plane is rotated about the C(21)-C(22) bond, so that the dihedral angle with the aromatic plane is 2.4°. This angle is considerably smaller than the corresponding values observed in the two previously described structures (8 and 12°). The ester group, attached to ring A, is in the equatorial position. Mathieson (1965) noted that in analogous structures the ester group was oriented so that it was coplanar with the hydrogen atom attached to the carbon atom in the ring (here C(2)). In this structure the ester group is rotated about the O(2)-C(2) bond by 43.3° from the position predicted by Mathieson. This orientation may be due to the intermolecular hydrogen bond between O(6) and O(4) which is energetically favoured.

In the ester group the C(21)-O(6) bond (1.142 Å) is much shorter than the value given by Sutton (1965) for carboxylic acids and esters. However, Sutton's value does not agree with the values in various esters listed below.



ℓ_1	ℓ_2	ℓ_3	Compound
1.206 Å	1.335 Å	1.490 Å)	a
1.224	1.336	1.462)	
1.164	1.348	1.455	b
1.190	1.372		c
1.221	1.337	1.472	d
1.223	1.351	1.459	e
1.196	1.360	1.476	f
1.188	1.343	1.463	g
1.200	1.347	1.533	h
1.196	1.398	1.420	i
1.201	1.355	1.470	mean value
1.142	1.333	1.472	ε-caesalpin
1.233	1.312		Sutton (1965)

a Reserpine (Karle and Karle, 1968)

b L-5-Methoxycarbonyl-7-formyl-1,2,5,6-tetrahydro-3H-pyrrolo [1,2-a] azepine-3-one (Karle, Karle, and Estlin, 1967)

c 2,7-Diacetoxy-*trans*-15,16-dimethyl-15,16-dihydropyrene (Hanson, 1965)

d Ethyl carbamate (Bracher and Small, 1967)

e *dℓ*-Alphaprodine HCℓ (Kartha, Ahmed, and Barnes, 1960)

f *dℓ*-Betaprodine HCℓ (Ahmed and Barnes, 1963)

g *dℓ*-Betaprodine HBr (Ahmed, Barnes, and Masironi, 1963)

h Taxadienetetraol derivative

i p-Bromophenacyl labdanolate

The C(21)-O(6) (1.142 Å) bond length differs significantly also from the mean value (1.201 Å) for the C=O bond in these esters. The atom O(6) vibrates highly anisotropically. The largest principal value of the vibration tensor (0.1000 $Å^2$) is approximately normal to the C(21)-O(6) bond, and this may explain the shortened bond. The C(2)-O(2) bond length (1.472 Å) is in very good agreement with the average C-O(C) bond (1.470 Å) in the esters listed above; it is longer than the C-O(H) bonds in this structure.

Two carbon-carbon single bonds, C(4)-C(5) (1.603 Å) and C(9)-C(10) (1.591 Å), are longer than the usual value of 1.537 ± 0.005 Å (Sutton, 1965). The former bond is between two fully substituted carbon atoms while the latter joins a tetra-substituted carbon atom to a tri-substituted one. Due to steric hindrance lengthening of bonds between highly substituted carbon atoms has been observed in various structures, e.g. 1.660 ± 0.022 and 1.646 ± 0.025 Å in methyl melaleucate iodoacetate (Hall and Maslen, 1965), 1.614 ± 0.023 Å in dimethylacetylene dicarboxylate indene adduct (Muir, 1967), and 1.627 ± 0.028 Å in davallol iodoacetate (Oh and Maslen, 1966).

Since no correction for anomalous dispersion was made an error in the y coordinate of the bromine atom is expected (Cruickshank and McDonald, 1967) and may cause the significant

deviation in the Br-C(25) bond length (1.905 Å) from the reported value 1.85 ± 0.01 Å (Sutton, 1965).

8. Hydrogen bonding

The molecular arrangement parallel to (010) can be seen in Figure 4.5, where the hydrogen bonds are marked with broken lines. The hydrogen bonds involving atoms O(1) and O(4) in equivalent position I are between these atoms and the atoms O(4) and O(1), respectively, in two different molecules in equivalent position III, the former at y+½, the latter at y-½. Similarly, O(4) and O(6) in equivalent position I are, respectively, connected to O(6) and O(4) in equivalent position II belonging to the molecules at y-½ and y+½, respectively. All the hydroxyl groups are involved in hydrogen bonding; one in an intramolecular (O(3)-H...O(1)) and two in intermolecular ($O(1)_I$-H...$O(4)_{III}$, $O(4)_I$-H...$O(6)_{II}$) bonds. Each molecule is thus connected with four neighbouring ones. The crystal structure can be described as consisting of spirals formed by the molecules which are joined by hydrogen bonds. The molecules connected in this way form sheets parallel to (001). This agrees with the fact that the crystals are plates with (001) as the predominant face.

Although the hydrogen positions were not determined,

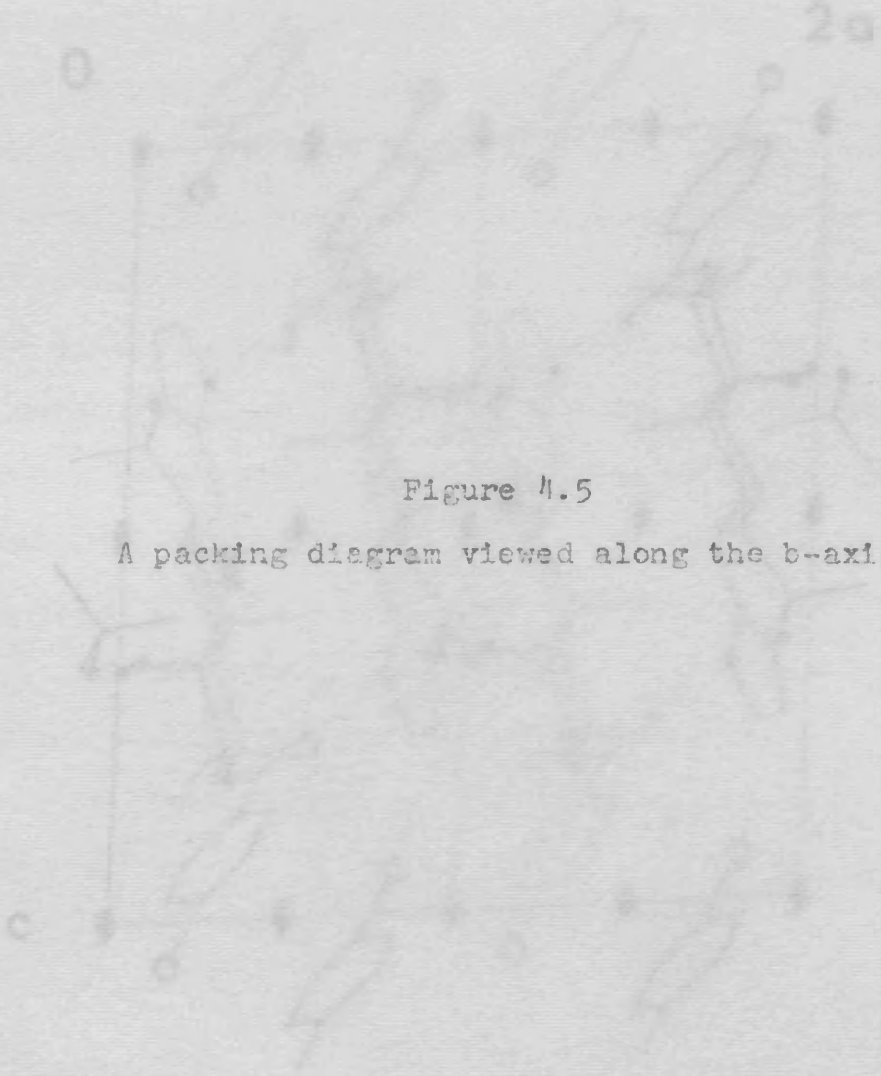
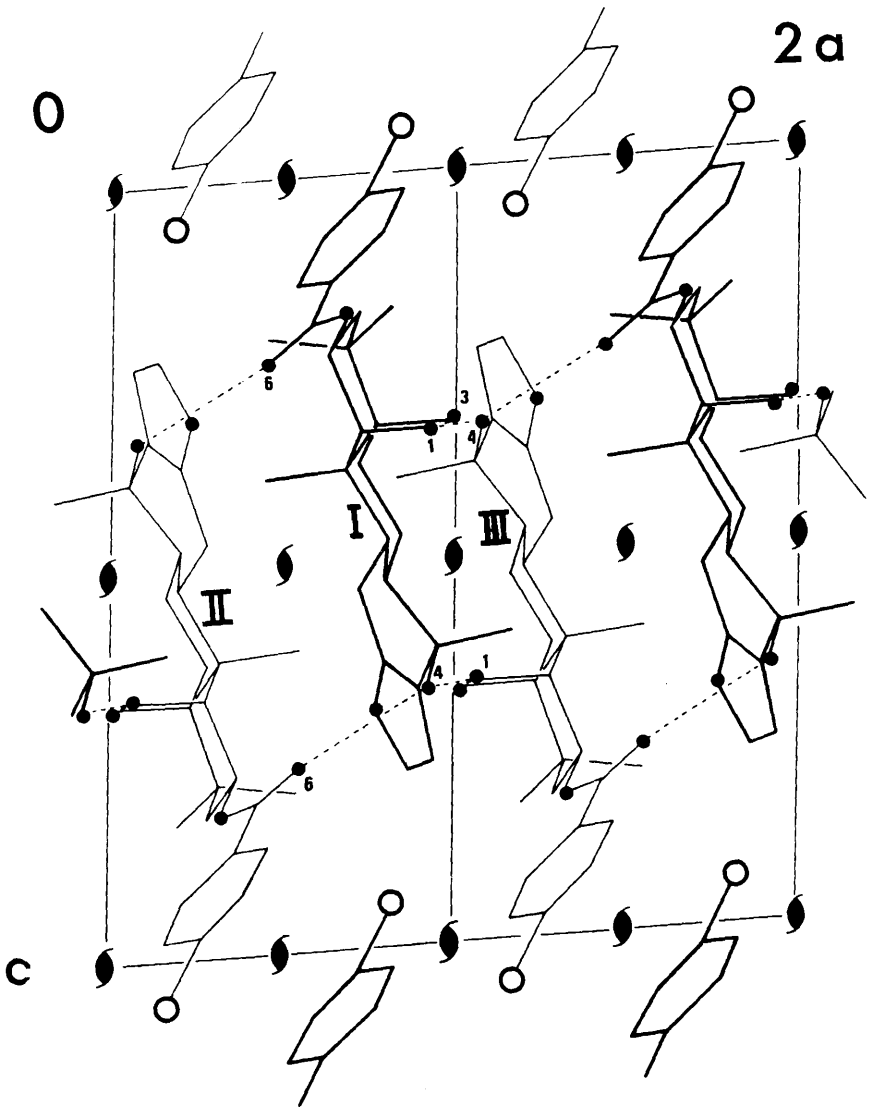


Figure 4.5

A packing diagram viewed along the b-axis.


0
2a
c
I
II
III
1
3
4
6

the donor-acceptor scheme can be unequivocally deduced from the fact that O(6) can only accept a proton. The oxygen atoms O(1) and O(4) act both as donors and as acceptors while O(3) acts only as a donor. The hydrogen bond lengths and angles with their e.s.d.'s are listed in Table 4.9. The bond lengths are all normal, the intramolecular bond being the shortest one. Due to the restrictions imposed on the axially bonded hydroxyl groups the C-O...O angle for the intramolecular bond is considerably smaller than those for the intermolecular bonds. From a survey of hydrogen bonds Fuller (1959) observed that they can deviate by as much as 20° from being linear. In view of this, all the C-O...O angles are normal.

All intermolecular distances <4.0 Å were calculated. Except for the hydrogen bonds mentioned above none of them is shorter than van der Waals distances.

TABLE 4.9

HYDROGEN BOND LENGTHS AND ANGLES WITH E.S.D.'s

(a) Intramolecular

Bond	Distance	Angle		Type
O(3)-H...O(1)	2.649 ± 11 Å	C(5)-O(3)...O(1)	87.7 ± 0.5°	(O-H...OH)

(b) Intermolecular

Bond	Distance	Angle		Type
$O(1)_I$-H...$O(4)_{III}$	2.738 ± 10 Å	C(1) -O(1)...O(4)	118.0 ± 0.5°	(O-H...OH)
$O(4)_I$-H...$O(6)_{II}$	2.812 ± 9	C(14)-O(4)...O(6)	124.8 ± 0.5	(O-H...O=C)

The subscripts refer to the equivalent positions:

I (x, y, z)

II (1-x,y-½,1-z)

III (2-x,y+½,1-z)

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